

DECLARATION

I, Ippei Andoh, having an address of c/o CHEMPATENT, LTD., Tamura Bldg. 5th Floor, 4-23-17, Higashi-Ikebukuro, Toshima-ku, Tokyo, Japan, hereby declare that I have competent knowledge of the Japanese and English languages, and that I have made the accompanying translation of JAPANESE PATENT APPLICATION NO. 2000-182297 filed on June 16, 2000[✓] in the name of JSR Corporation, and that the said translation is true and correct to the best of my knowledge and belief and that this declaration was made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code.

DECLARED by said Ippei Andoh

at Tamura Bldg. 5th Floor, 4-23-17, Higashi-Ikebukuro, Toshima-ku,
Tokyo, Japan

This 13th day of June, 2003


Ippei Andoh

**PATENT OFFICE
JAPANESE GOVERNMENT**

This is to certify that the annexed is a true copy of the following application as filed with this Office.

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[Inventor]
 [Address] c/o JSR Corporation
 2-11-24, Tsukiji, Chuo-ku, Tokyo
 [Name] Yukio NISHIMURA
[Inventor]
 [Address] c/o JSR Corporation
 2-11-24, Tsukiji, Chuo-ku, Tokyo
 [Name] Noboru YAMAHARA
[Inventor]
 [Address] c/o JSR Corporation
 2-11-24, Tsukiji, Chuo-ku, Tokyo
 [Name] Masafumi YAMAMOTO
[Inventor]
 [Address] c/o JSR Corporation
 2-11-24, Tsukiji, Chuo-ku, Tokyo
 [Name] Toru KAJITA
[Inventor]
 [Address] c/o JSR Corporation
 2-11-24, Tsukiji, Chuo-ku, Tokyo
 [Name] Tsutomu SHIMOKAWA
[Applicant for Patent]
 [Identification No.] 000004178

| | |
|--|-------------------|
| [Name] | JSR Corporation |
| [Representative] | Eiichi MATSUMOTO |
| [Agent] | |
| [Identification No.] | 100100985 |
| [Patent Attorney] | |
| [Name] | Toshiaki FUKUZAWA |
| [Telephone No.] | 03-5570-2185 |
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| [Successor] | |
| [Identification No.] | 390009531 |
| [Name] | INTERNATIONAL BUSINESS MACHINES CORPORATION |
| [Representative] | Jeffrey L. Forman |
| [Successor's Agent] | |
| [Identification No.] | 100100985 |
| [Patent Attorney] | |
| [Name] | Toshiaki FUKUZAWA |
| [Telephone No.] | 03-5570-2185 |
| [Assignor] | |
| [Identification No.] | 000004178 |
| [Name] | JSR Corporation |
| [Representative] | Eiichi MATSUMOTO |
| [Assignor's Agent] | |
| [Identification No.] | 100100985 |
| [Patent Attorney] | |
| [Name] | Toshiaki FUKUZAWA |
| [Telephone No.] | 03-5570-2185 |
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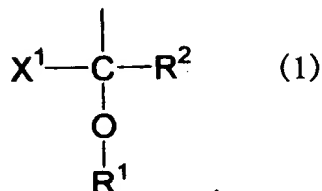
[Document Name] Specification

[Title of the Invention] RADIATION-SENSITIVE RESIN COMPOSITION

[Claims]

[Claim 1] A radiation-sensitive resin composition comprising (A) an acid-dissociating group-containing resin having a structure represented by the following formula (1) and (B) a photoacid generator:

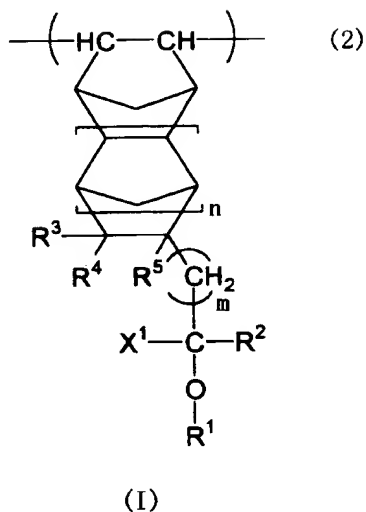
[Formula 1]



wherein R¹ represents a hydrogen atom, a monovalent acid-dissociating group, an alkyl group having 1-6 carbon atoms which does not have an acid-dissociating group, or an alkylcarbonyl group having 2-7 carbon atoms which does not have an acid-dissociating group, X¹ represents a linear or branched fluorinated alkyl group having 1-4 carbon atoms, and R² represents a hydrogen atom, a linear or branched alkyl group having 1-10 carbon atoms, or a linear or branched fluorinated alkyl group having 1-10 carbon atoms.

[Claim 2] A radiation-sensitive resin composition comprising (A) an acid-dissociating group-containing resin having a recurring unit (I) represented by the following formula (2) and (B) a photoacid generator:

[Formula 2]

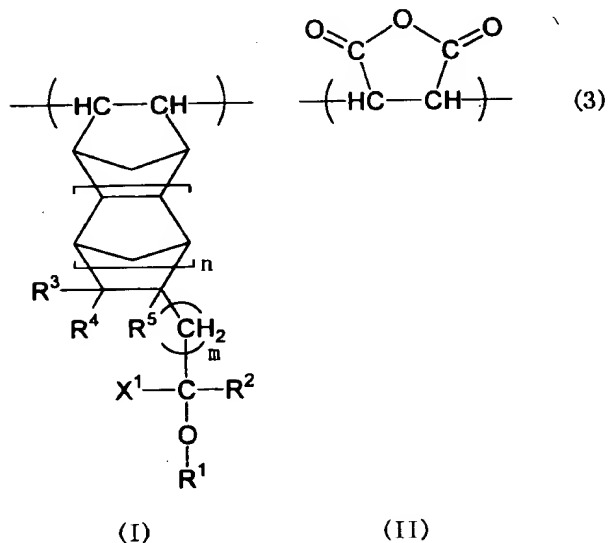


wherein R¹ represents a hydrogen atom, a monovalent acid-dissociating group, an alkyl group having 1-6 carbon atoms which does not have an acid-dissociating group, or an alkylcarbonyl group having 2-7 carbon atoms which does not have an acid-dissociating group, X¹ represents a linear or branched fluorinated alkyl group having 1-4 carbon atoms, R² represents a hydrogen atom, a linear or branched alkyl group having 1-10 carbon atoms, or a linear or branched fluorinated alkyl group having 1-10 carbon atoms, R³, R⁴, and R⁵ individually represent a hydrogen atom or a linear or branched alkyl group having 1-4 carbon atoms, a monovalent oxygen-containing polar group, or a monovalent nitrogen-containing polar group, n is an integer of 0-2, and m is an integer of 0-3.

[Claim 3] A radiation-sensitive resin composition comprising (A) an alkali insoluble or scarcely soluble

acid-dissociating group-containing resin having a recurring unit (I) and a recurring unit (II) shown by the following formula (3) and (B) a photoacid generator:

[Formula 3]

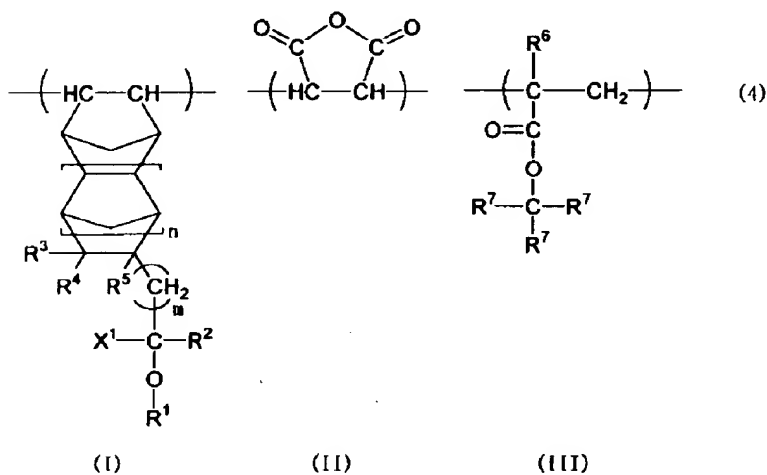


wherein R^1 represents a hydrogen atom, a monovalent acid-dissociating group, an alkyl group having 1-6 carbon atoms which does not have an acid-dissociating group, or an alkylcarbonyl group having 2-7 carbon atoms which does not have an acid-dissociating group, X^1 represents a linear or branched fluorinated alkyl group having 1-4 carbon atoms, R^2 represents a hydrogen atom, a linear or branched alkyl group having 1-10 carbon atoms, or a linear or branched fluorinated alkyl group having 1-10 carbon atoms, R^3 , R^4 , and R^5 individually represents a hydrogen atom or a linear or branched alkyl group having 1-4 carbon atoms, a monovalent oxygen-containing polar group, or

a monovalent nitrogen-containing polar group, n is an integer of 0-2, and m is an integer of 0-3.

[Claim 4] The radiation-sensitive resin composition according to claim 3, wherein the alkali insoluble or scarcely soluble acid-dissociating group-containing resin (A) has a recurring unit (I), recurring unit (II), and recurring unit (III) shown by the following formula (4):

[Formula 4]

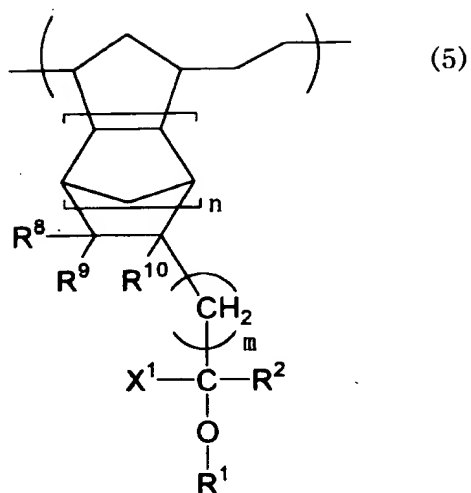


wherein R¹ represents a hydrogen atom, a monovalent acid-dissociating group, an alkyl group having 1-6 carbon atoms which does not have an acid-dissociating group, or an alkylcarbonyl group having 2-7 carbon atoms which does not have an acid-dissociating group, X¹ represents a linear or branched fluorinated alkyl group having 1-4 carbon atoms, R² represents a hydrogen atom, a linear or branched alkyl group having 1-10 carbon atoms, or a linear or branched fluorinated alkyl group having 1-10 carbon atoms, R³, R⁴, and R⁵ individually represent

a hydrogen atom or a linear or branched alkyl group having 1-4 carbon atoms, a monovalent oxygen-containing polar group, or a monovalent nitrogen-containing polar group, n is an integer of 0-2, m is an integer of 0-3, R⁶ represents a hydrogen atom or methyl group, and R⁷ individually represents a linear or branched alkyl group having 1-4 carbon atoms or a monovalent alicyclic hydrocarbon group having 4-20 carbon atoms or a derivative thereof, or any two of R⁷s form in combination with a carbon atom to which each R⁷ bonds, a divalent alicyclic hydrocarbon group having 4-20 carbon atoms or a derivative thereof, with the remaining R⁷ being a linear or branched alkyl group having 1-4 carbon atoms or a monovalent alicyclic hydrocarbon group having 4-20 carbon atoms or a derivative thereof.

[Claim 5] A radiation-sensitive resin composition comprising (A) an acid-dissociating group-containing resin having a recurring unit (IV) represented by the following formula (5) and (B) a photoacid generator:

[Formula 5]



(IV)

wherein R^1 represents a hydrogen atom, a monovalent acid-dissociating group, an alkyl group having 1-6 carbon atoms which does not have an acid-dissociating group, or an alkylcarbonyl group having 2-7 carbon atoms which does not have an acid-dissociating group, X^1 represents a linear or branched fluorinated alkyl group having 1-4 carbon atoms, R^2 represents a hydrogen atom, a linear or branched alkyl group having 1-10 carbon atoms, or a linear or branched fluorinated alkyl group having 1-10 carbon atoms, R^8 , R^9 , and R^{10} individually represent a hydrogen atom or a linear or branched alkyl group having 1-4 carbon atoms, a monovalent oxygen-containing polar group, or a monovalent nitrogen-containing polar group, n is an integer of 0-2, and m is an integer of 0-3.

[0001]

[Field of the Invention]

The present invention relates to a radiation-sensitive

resin composition and, more particularly, to a radiation-sensitive resin composition suitable as a chemically-amplified resist useful for microfabrication utilizing various types of radiation, for example, deep ultraviolet rays such as a KrF excimer laser or ArF excimer laser, X-rays such as synchrotron radiation, or charged particle rays such as electron beams.

[0002]

[Prior Art]

In the field of microfabrication represented by fabrication of integrated circuit devices, a lithographic technology enabling microfabrication with a line width of 0.20 μm or less has been demanded in order to achieve a higher degree of integration.

A conventional lithographic process generally utilizes near ultraviolet rays such as i-line as radiation. It is known in the art that microfabrication with a line width of sub-quarter micron is very difficult using near ultraviolet rays.

Therefore, use of radiation with a shorter wavelength has been studied for enabling microfabrication with a line width of 0.20 μm or less. As examples of radiation with a shorter wavelength, deep ultraviolet rays represented by a bright line spectrum of a mercury lamp and an excimer laser, X-rays, electron beams, and the like can be given. Of these, a KrF excimer laser (wavelength: 248 nm) and an ArF excimer laser (wavelength: 193 nm) have attracted attention.

As a radiation-sensitive resin composition applicable to the excimer laser radiation, a number of compositions utilizing a chemical amplification effect between a component having an acid-dissociating functional group and a component generating an acid (hereinafter called "photoacid generator") which generates an acid upon irradiation (hereinafter called "exposure") has been proposed. Such a composition is hereinafter called a chemically-amplified radiation-sensitive composition.

As examples of the chemically-amplified radiation-sensitive composition, Japanese Patent Publication No. 27660/1990 discloses a composition comprising a polymer containing a t-butyl ester group of carboxylic acid or a t-butylcarbonate group of phenol and a photoacid generator. This composition utilizes the effect of the polymer to release a t-butyl ester group or t-butyl carbonate group by the action of an acid generated upon exposure to form an acidic group such as a carboxylic group or a phenolic hydroxyl group, which renders an exposed area on a resist film readily soluble in an alkaline developer.

[0003]

Most of conventional chemically-amplified radiation-sensitive compositions use a phenol resin as a base resin. Deep ultraviolet rays used as radiation for exposure are absorbed due to an aromatic ring in the resin and cannot sufficiently reach the bottom of the resist film. Because of this, the dose of the radiation is greater at the film surface

and is smaller at the bottom of the resist film. This causes critical dimension of a resist pattern to be smaller at the film surface and be larger toward the bottom, thereby forming a tapered profile after development. No sufficient resolution can be obtained from such a resist film. Such a tapered profile formed after development cannot give a desired dimensional accuracy in the succeeding steps such as an etching step and an ion implantation step. In addition, if the configuration of the resist pattern is not rectangular on the upper portion, the resist disappears faster during dry etching, making it difficult to control etching conditions.

The resist profile can be improved by increasing the radiation transmittance through the resist film. For example, (meth)acrylate resins represented by polymethylmethacrylate are desirable from the viewpoint of radiation transmittance due to the superior transparency to deep ultraviolet rays. Japanese Patent Application Laid-open No. 226461/1992 proposes a chemically-amplified radiation-sensitive resin composition using a methacrylate resin. However, in spite of the excellent micro-processing performance, this composition exhibits only poor dry etching resistance due to the absence of an aromatic ring, giving rise to difficulty in performing etching with high accuracy. This composition thus does not have both radiation transmittance and dry etching resistance at the same time.

[0004]

A method of introducing an alicyclic ring into the resin component in the composition instead of an aromatic ring has

been known as a means for improving dry etching resistance without impairing radiation transmittance of the resist made from a chemically-amplified radiation-sensitive resin composition. A chemically-amplified radiation-sensitive resin composition using a (meth)acrylate resin having an alicyclic ring is proposed in Japanese Patent Application Laid-open No. 234511/1995, for example.

This composition, however, comprises groups which are comparatively easily dissociated with conventional acids (for example, an acetal functional group such as a tetrahydropyranyl group) and groups which are comparatively difficult to be dissociated with acids (for example, a t-butyl functional group such as a t-butyl ester group, t-butylcarbonate group) as an acid-dissociating functional group in the resin component. The resin component possessing the former acid-dissociating functional group exhibits excellent basic characteristics as a resist such as superior sensitivity and excellent pattern shape, but has a problem of poor storage stability, whereas the resin component possessing the latter acid-dissociating functional group exhibits impaired resist characteristics, particularly in terms of sensitivity and pattern shape, in spite of excellent storage stability. In addition, inclusion of an alicyclic structure in the resin components of this composition increases hydrophobicity of the resin, resulting in poor adhesion to substrates.

In view of recent progress in the microfabrication of semiconductor devices, development of a novel resin component

exhibiting high transmittance of radiation, having excellent basic properties as a resist, and suitable for use in chemically amplified radiation sensitive compositions which can be adapted to short wavelength radiation represented by deep ultraviolet rays is an important subject.

[0005]

[Problems to be Solved by the Invention]

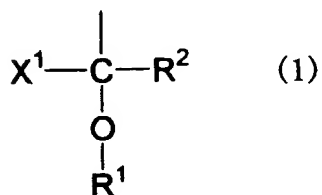
Therefore, an object of the present invention is to provide a novel radiation-sensitive resin composition, which has high transmittance of radiation, exhibits superior basic properties as a resist such as high sensitivity, resolution, and pattern shape, and is capable of producing semiconductors at a high yield without producing developing defects during microfabrication.

[0006]

[Means for Solving the Problems]

The above object can be achieved in the present invention by a radiation-sensitive resin composition comprising (A) an acid-dissociating group-containing resin having a structure represented by the following formula (1) and (B) a photoacid generator:

[Formula 6]



wherein R^1 represents a hydrogen atom, a monovalent acid-dissociating group, an alkyl group having 1-6 carbon atoms which does not have an acid-dissociating group, or an alkylcarbonyl group having 2-7 carbon atoms which does not have an acid-dissociating group, X^1 represents a linear or branched fluorinated alkyl group having 1-4 carbon atoms, and R^2 represents a hydrogen atom, a linear or branched alkyl group having 1-10 carbon atoms, or a linear or branched fluorinated alkyl group having 1-10 carbon atoms.

[0007]

The present invention will be described in detail below.

Component (A)

The component (A) of the present invention is an acid-dissociating group-containing resin (hereinafter referred to as "resin (A)") represented by the structure shown in the above formula (1) (hereinafter referred to as "structure (1)").

The radiation-sensitive resin composition of the present invention, as a chemically-amplified resist, exhibits excellent solubility in a developer and produces no developing effects due to possession of the structure (1) by the resin (A).

[0008]

As examples of the monovalent acid-dissociating group represented by R^1 (hereinafter referred to as an "acid-dissociating group (i)"), a tertiary alkyl group, acetal group, substituted methyl group, 1-substituted ethyl group,

1-substitution propyl group, 1-branched alkyl group (excluding tertiary alkyl groups), silyl group, germyl group, alkoxy carbonyl group, acyl group, cyclic acid-dissociating group, and the like can be given.

[0009]

As examples of the tertiary alkyl group in the acid-dissociating group (i), a t-butyl group, 1,1-dimethylpropyl group, 1-methyl-1-ethylpropyl group, 1,1-dimethylbutyl group, 1-methyl-1-ethylbutyl group, 1,1-dimethylpentyl group, 1-methyl-1-ethylpentyl group, 1,1-dimethylhexyl group, 1,1-dimethylheptyl group, 1,1-dimethyloctyl group, and the like can be given.

As examples of the acetal group, a methoxymethoxy group, ethoxymethoxy group, n-propoxymethoxy group, i-propoxymethoxy group, n-butoxymethoxy group, t-butoxymethoxy group, n-pentyloxymethoxy group, n-hexyloxymethoxy group, cyclopentyloxymethoxy group, cyclohexyloxymethoxy group, 1-methoxyethoxy group, 1-ethoxyethoxy group, 1-n-propoxyethoxy group, 1-i-propoxyethoxy group, 1-n-butoxyethoxy group, 1-t-butoxyethoxy group, 1-n-pentyloxyethoxy group, 1-n-hexyloxyethoxy group, 1-cyclopentyloxyethoxy group, 1-cyclohexyloxyethoxy group, (cyclohexyl) (methoxy) methoxy group, (cyclohexyl) (ethoxy) methoxy group, (cyclohexyl) (n-propoxy) methoxy group, (cyclohexyl) (i-propoxy) methoxy group, (cyclohexyl) (cyclohexyloxy) methoxy group, and the like can be

given.

[0010]

As examples of the substituted methyl group, a methoxymethyl group, methylthiomethyl group, ethoxymethyl group, ethylthiomethyl group, methoxyethoxymethyl group, benzyloxymethyl group, benzylthiomethyl group, phenacyl group, bromophenacyl group, methoxyphenacyl group, methylthiophenacyl group, α -methylphenacyl group, cyclopropylmethyl group, benzyl group, diphenylmethyl group, triphenylmethyl group, bromobenzyl group, nitrobenzyl group, methoxybenzyl group, methylthiobenzyl group, ethoxybenzyl group, ethylthiobenzyl group, piperonyl group, methoxycarbonylmethyl group, ethoxycarbonylmethyl group, n-propoxycarbonylmethyl group, i-propoxycarbonylmethyl group, n-butoxycarbonylmethyl group, t-butoxycarbonylmethyl group, and the like can be given.

As examples of the 1-substituted ethyl group, a 1-methoxyethyl group, 1-methylthioethyl group, 1,1-dimethoxyethyl group, 1-ethoxyethyl group, 1-ethylthioethyl group, 1,1-diethoxyethyl group, 1-phenoxyethyl group, 1-phenylthioethyl group, 1,1-diphenoxyethyl group, 1-benzyloxyethyl group, 1-benzylthioethyl group, 1-cyclopropylethyl group, 1-phenylethyl group, 1,1-diphenylethyl group, 1-methoxycarbonylethyl group, 1-ethoxycarbonylethyl group, 1-n-propoxycarbonylethyl group, 1-i-propoxycarbonylethyl group, 1-n-butoxycarbonylethyl group,

1-t-butoxycarbonylethyl group, and the like can be given.

As examples of the 1-substituted propyl group, a 1-methoxypropyl group, 1-ethoxypropyl group, and the like can be given.

[0011]

As examples of the 1-branched alkyl group, i-propyl group, sec-butyl group, 1-methylbutyl group, and the like can be given.

As examples of the silyl group, a trimethylsilyl group, ethyldimethylsilyl group, methyldiethylsilyl group, triethylsilyl group, i-propyldimethylsilyl group, methyldi-i-propylsilyl group, tri-i-propylsilyl group, t-butyldimethylsilyl group, methyldi-t-butylsilyl group, tri-t-butylsilyl group, phenyldimethylsilyl group, methyldiphenylsilyl group, triphenylsilyl group, and the like can be given.

As examples of the germyl group, a trimethylgermyl group, ethyldimethylgermyl group, methyldiethylgermyl group, triethylgermyl group, i-propyldimethylgermyl group, methyldi-i-propylgermyl group, tri-i-propylgermyl group, t-butyldimethylgermyl group, methyldi-t-butylgermyl group, tri-t-butylgermyl group, phenyldimethylgermyl group, methyldiphenylgermyl group, triphenylgermyl group, and the like can be given.

As examples of the alkoxycarbonyl group, a methoxycarbonyl group, ethoxycarbonyl group, i-propoxycarbonyl group, t-butoxycarbonyl group, and the like can be given.

[0012]

As examples of the acyl group, an acetyl group, propionyl group, butyryl group, heptanoyl group, hexanoyl group, valeryl group, pivaloyl group, isovaleryl group, lauroyl group, myristoyl group, palmitoyl group, stearoyl group, oxalyl group, malonyl group, succinyl group, glutaryl group, adipoyl group, piperoyl group, suberoyl group, azelaoyl group, sebacoyl group, acryloyl group, propioloyl group, methacryloyl group, crotonoyl group, oleoyl group, maleoyl group, fumaroyl group, mesaconoyl group, campholoyl group, benzoyl group, phthaloyl group, isophthaloyl group, terephthaloyl group, naphthoyl group, toluoyl group, hydroatropoyl group, atropoyl group, cinnamoyl group, furoyl group, thenoyl group, nicotinoyl group, isonicotinoyl group, p-toluenesulfonyl group, mesyl group, and the like can be given.

As examples of the cyclic acid-dissociating group, a 3-oxocyclohexyl group, tetrahydropyranyl group, tetrahydrofuranyl group, tetrahydrothiopyranyl group, tetrahydrothiofuranyl group, 3-bromotetrahydropyranyl group, 4-methoxytetrahydropyranyl group, 2-oxo-4-methyl-4-tetrahydropyranyl group, 4-methoxytetrahydrothiopyranyl group, 3-tetrahydrothiophene-1,1-dioxide group, and the like can be given.

[0013]

Of these acid-dissociating groups (i), a t-butyl group, 1-methoxyethoxy group, 1-ethoxyethoxy group,

1-cyclohexyloxyethoxy group, methoxymethyl group, t-butoxycarbonylmethyl group, 1-methoxyethyl group, 1-ethoxyethyl group, 1-n-propoxyethyl group, 1-cyclohexyloxyethyl group, 1-ethoxypropyl group, trimethylsilyl group, t-butoxycarbonyl group, tetrahydropyranyl group, tetrahydrofuranyl group, and the like are preferable.

[0014]

The alkyl group represented by R^1 having 1-6 carbon atoms and no acid-dissociating group may be linear, branched or cyclic, and the examples include a methyl group, ethyl group, n-propyl group, n-butyl group, i-butyl group, n-pentyl group, n-hexyl group, cyclopentyl group, and cyclohexyl group.

Of these alkyl groups, a methyl group, ethyl group, n-propyl group, and cyclohexyl group are particularly preferable.

[0015]

The alkylcarbonyl group represented by R^1 having 2-7 carbon atoms and no acid-dissociating group may be linear, branched, or cyclic, and the examples include a methylcarbonyl group, ethylcarbonyl group, n-propylcarbonyl group, n-butylcarbonyl group, i-butylcarbonyl group, n-pentylcarbonyl group, i-pentylcarbonyl group, n-hexylcarbonyl group, i-hexylcarbonyl group, and cyclohexylcarbonyl group.

Of these alkylcarbonyl groups, a methylcarbonyl group, ethylcarbonyl group, and the like are particularly preferable.

[0016]

Particularly preferable groups for R^1 in the formula (1) are a hydrogen atom, the above-mentioned preferable acid-dissociating groups (i), a methyl group, ethyl group, methylcarbonyl group, ethylcarbonyl group, and the like.

[0017]

Given as examples of the linear or the branched fluoro alkyl group having 1-4 carbon atoms represented by X^1 are a fluoromethyl group, difluoromethyl group, perfluoromethyl group, 1-fluoroethyl group, 1,1-difluoroethyl group, 2,2,2-trifluoroethyl group, perfluoroethyl group, 1-fluoro-n-propyl group, 1,1-difluoro-n-propyl group, 3,3,3-trifluoro-n-propyl group, 3,3,3,2,2-pentafluoro-n-propyl group, perfluoro-n-propyl group, 1-fluoro-1-methylethyl group, 2-trifluoro-1-methylethyl group, perfluoro-i-propyl group, 1-fluoro-n-butyl group, 1,1-difluoro-n-butyl group, 4,4,4-trifluoro-n-butyl group, 4,4,4,3,3-pentafluoro-n-butyl group, 4,4,4,3,3,2,2-heptafluoro-n-butyl group, perfluoro-n-butyl group, and the like.

Of these fluoroalkyl groups, a fluoromethyl group, difluoromethyl group, perfluoromethyl group, 1,1-difluoroethyl group, 2,2,2-trifluoroethyl group, 1-fluoro-1-methylethyl group, and the like are preferable.

[0018]

Given as examples of the linear or the branched alkyl group having 1-10 carbon atoms represented by R^2 are a methyl

group, ethyl group, n-propyl group, i-propyl group, n-butyl group, i-butyl group, sec-butyl group, t-butyl group, n-pentyl group, neopentyl group, n-hexyl group, n-heptyl group, n-octyl group, 2-ethylhexyl group, n-nonyl group, n-decyl group, and the like.

Of these, a methyl group, ethyl group, n-propyl group, n-hexyl group, and the like are preferable.

[0019]

Given as examples of the linear or the branched fluoroalkyl group having 1-10 carbon atoms represented by R^2 are a fluoromethyl group, difluoromethyl group, perfluoromethyl group, 1-fluoroethyl group, 1,1-difluoroethyl group, 2,2,2-trifluoroethyl group, perfluoroethyl group, 1-fluoro-n-propyl group, 1,1-difluoro-n-propyl group, 3,3,3-trifluoro-n-propyl group, 3,3,3,2,2-pentafluoro-n-propyl group, perfluoro-n-propyl group, 1-fluoro-1-methylethyl group, 2-trifluoro-1-methylethyl group, perfluoro-i-propyl group, 1-fluoro-n-butyl group, 1,1-difluoro-n-butyl group, 4,4,4-trifluoro-n-butyl group, 4,4,4,3,3-pentafluoro-n-butyl group, 4,4,4,3,3,2,2-heptafluoro-n-butyl group, perfluoro-n-butyl group, 2-fluoro-2-methylpropyl group, 1-fluoro-1-methylpropyl group, 1-fluoro-n-pentyl group, 1,1-difluoro-n-pentyl group, 5,5,5-trifluoro-n-pentyl group, 1-fluoro-n-hexyl group, 1,1-difluoro-n-hexyl group, 6,6,6-trifluoro-n-hexyl group, 1-fluoro-n-heptyl group, 1,1-difluoro-n-heptyl group, 7,7,7-trifluoro-n-heptyl group,

1-fluoro-n-octyl group, 1,1-difluoro-n-octyl group, 8,8,8-trifluoro-n-octyl group, 2-fluoro-2-ethylhexyl group, 1-fluoro-n-nonyl group, 1,1-difluoro-n-nonyl group, 9,9,9-trifluoro-n-nonyl group, 1-fluoro-n-decyl group, 1,1-difluoro-n-decyl group, and 10,10,10-trifluoro-n-decyl group.

Of these fluoroalkyl groups, a fluoromethyl group, difluoromethyl group, perfluoromethyl group, 1,1-difluoroethyl group, 2,2,2-trifluoroethyl group, 1-fluoro-1-methylethyl group, and the like are preferable.

[0020]

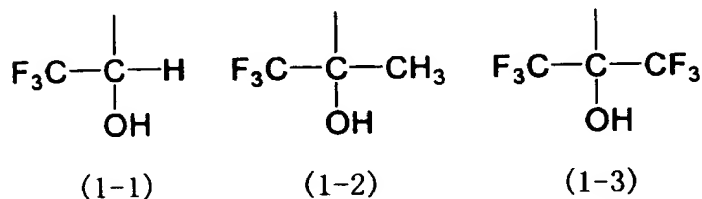
Particularly preferable groups for R² in the formula (2) are a hydrogen atom, methyl group, perfluoromethyl group, and the like.

[0021]

Specific preferable examples of the structure (1) include the structures of the following formulas (1-1) to (1-12).

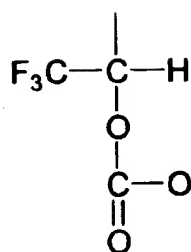
[0022]

[Formula 7]

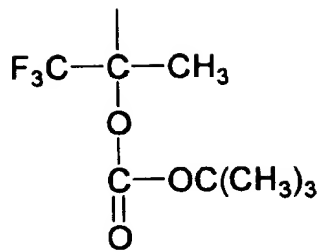


[0023]

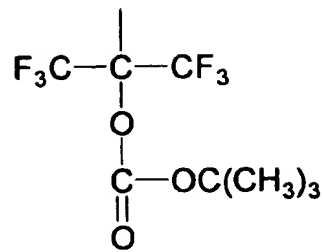
[Formula 8]



(1-4)



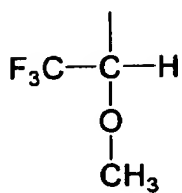
(1-5)



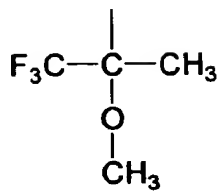
(1-6)

[0024]

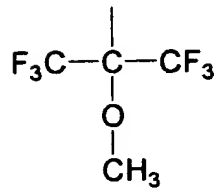
[Formula 9]



(1-7)



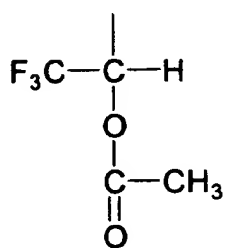
(1-8)



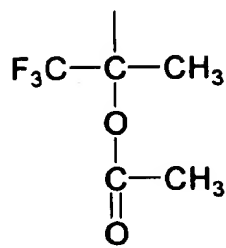
(1-9)

[0025]

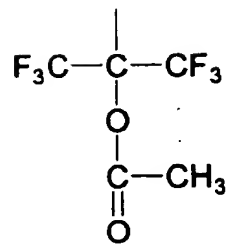
[Formula 10]



(1-10)



(1-11)



(1-12)

[0026]

Of these, the structures shown by the formulas (1-3), (1-6), (1-12), and the like are preferable.

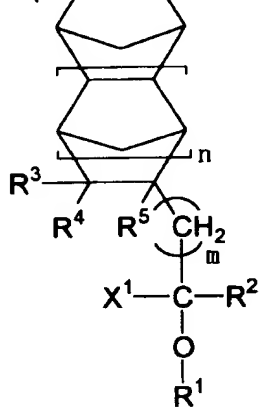
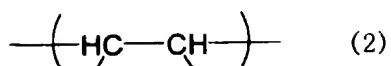
[0027]

Any resins including addition condensation resins, polyaddition resins, ring-opening polymerization resins, condensation polymerization resins, and the like can be employed without specific limitations as the resin (A) inasmuch as the resin has an acid-dissociating group represented by the structure (1). From the viewpoint of transmittance of radioactive rays and the like, the resin (A) of the present invention preferably does not have an aromatic ring or contains as small an amount of aromatic rings as possible.

As preferable specific examples of the resin (A) in the present invention, an acid-dissociating group-containing resin having a recurring unit (I) shown by the following formula (2) (hereinafter referred to as "resin (A1)"), an acid-dissociating group-containing resin having a structural unit (IV) shown by the following formula (5) (hereinafter referred to as "resin (A2)"), and the like can be given:

[0028]

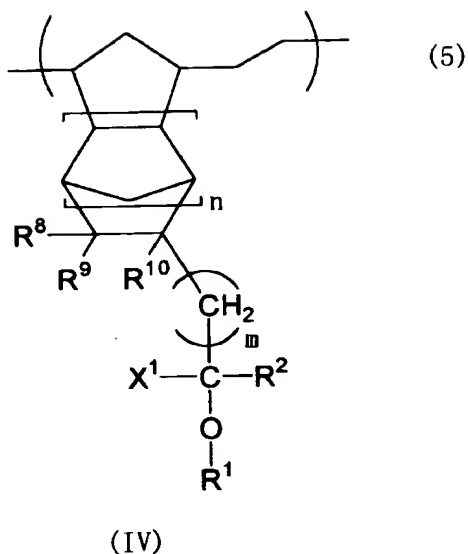
[Formula 11]



wherein R^1 , X^1 , and R^2 are the same as defined for the above formula (1), R^3 , R^4 , and R^5 individually represents a hydrogen atom or a linear or branched alkyl group having 1-4 carbon atoms, a monovalent oxygen-containing polar group, or a monovalent nitrogen-containing polar group, n is an integer of 0-2, and m is an integer of 0-3,

[0029]

[Formula 12]



wherein R^1 , X^1 , and R^2 are the same as defined for the above formula (1), R^8 , R^9 , and R^{10} individually represents a hydrogen atom or a linear or branched alkyl group having 1-4 carbon atoms, a monovalent oxygen-containing polar group, or a monovalent nitrogen-containing polar group, n is an integer of 0-2, and m is an integer of 0-3.

[0030]

First, the resin (A1) will be explained.

As examples of the linear or branched alkyl group having 1-4 carbon atoms represented by R^3 , R^4 , or R^5 in the formula (2), a methyl group, ethyl group, n-propyl group, i-propyl group, n-butyl group, i-butyl group, sec-butyl group, t-butyl group, and the like can be given.

Of these alkyl groups, a methyl group, ethyl group, and the like are particularly preferable.

[0031]

As examples of the monovalent oxygen-containing polar group represented by R^3 , R^4 , or R^5 , a hydroxyl group; carboxyl group; linear or branched hydroxyalkyl groups having 1-4 carbon atoms such as a hydroxymethyl group, 1-hydroxyethyl group, 2-hydroxyethyl group, 1-hydroxy-n-propyl group, 2-hydroxy-n-propyl group, 3-hydroxy-n-propyl group, 1-hydroxy-n-butyl group, 2-hydroxy-n-butyl group, 3-hydroxy-n-butyl group, and 4-hydroxy-n-butyl group; and linear or branched alkoxy groups having 1-4 carbon atoms such as a methoxy group, ethoxy group, n-propoxy group, i-propoxy group, n-butoxy group, 2-methylpropoxy group, 1-methylpropoxy group, t-butoxy group, and the like can be given.

Of these oxygen-containing polar groups, a hydroxyl group, carboxyl group, hydroxymethyl group, methoxy group, ethoxy group, and the like are preferable.

[0032]

As examples of the monovalent nitrogen-containing polar group represented by R^3 , R^4 , or R^5 , a cyano group; linear or branched cyanoalkyl groups having 2-5 carbon atoms such as a cyanomethyl group, 1-cyanoethyl group, 2-cyanoethyl group, 1-cyano-n-propyl group, 2-cyano-n-propyl group, 3-cyano-n-propyl group, 1-cyano-n-butyl group, 2-cyano-n-butyl group, 3-cyano-n-butyl group, 4-cyano-n-butyl group, and the like.

Of these nitrogen-containing polar groups, a cyano group, cyanomethyl group, 1-cyanoethyl group, and the like are preferable.

[0033]

Particularly preferable groups represented by R^3 , R^4 , or R^5 in the formula (2) are a hydrogen atom, methyl group, ethyl group, hydroxyl group, carboxyl group, hydroxymethyl group, methoxy group, ethoxy group, cyano group, cyanomethyl group, 1-cyanoethyl group, and the like.

m and n in the formula (2) are preferably either 0 or 1.

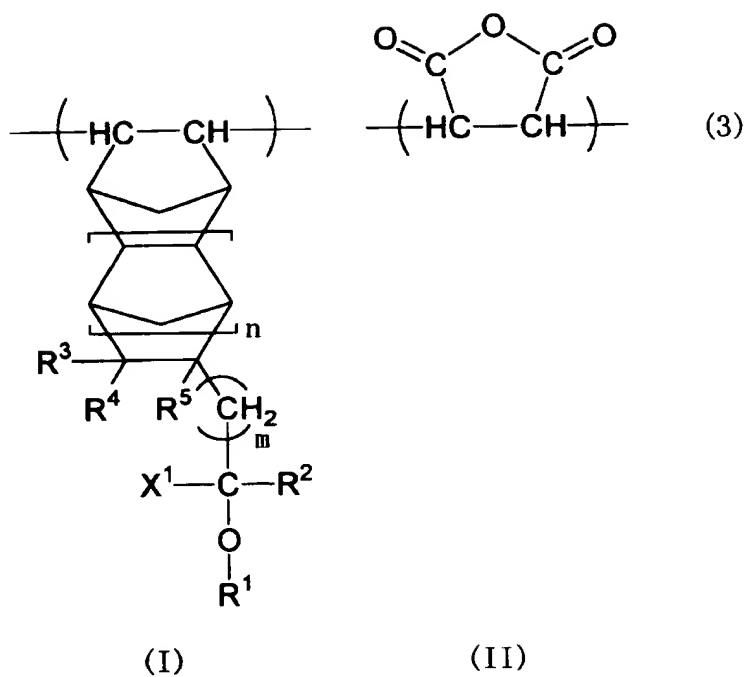
The recurring unit (I) may be present in the resin (A1) either individually or in combination of two or more.

[0034]

As preferable examples of the resin (A1) in the present invention, an alkali insoluble or scarcely alkali soluble acid-dissociating group-containing resin having the recurring unit (I) and recurring unit (II) shown by the following formula (3) (hereinafter referred to as "resin (A1-1)"), an alkali insoluble or scarcely alkali soluble acid-dissociating group-containing resin having the recurring unit (I), recurring unit (II), and recurring unit (III) shown by the following formula (4) (hereinafter referred to as "resin (A1-2)"), and the like can be given:

[0035]

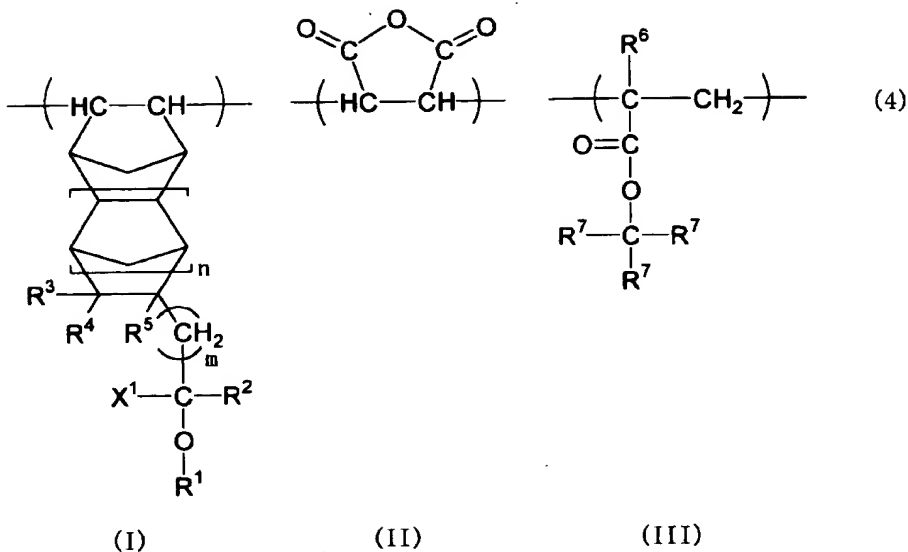
[Formula 13]



wherein R^1 , X^1 , and R^2 are the same as defined for the above formula (1), and R^3 , R^4 , R^5 , n , and m have the same meanings as defined for the corresponding symbols in the formula (2),

[0036]

[Formula 14]



wherein R^1 , X^1 , and R^2 are the same as defined for the above formula (1), R^3 , R^4 , R^5 , n , and m have the same meanings as defined for the corresponding symbols in the formula (2), R^6 represents a hydrogen atom or methyl group, and R^7 individually represents a linear or branched alkyl group having 1-4 carbon atoms or a monovalent alicyclic hydrocarbon group having 4-20 carbon atoms or a derivative thereof, or any two of R^7 's form in combination with a carbon atom to which each R^7 bonds, a divalent alicyclic hydrocarbon group having 4-20 carbon atoms or a derivative thereof, with the remaining R^7 being a linear or branched alkyl group having 1-4 carbon atoms or a monovalent alicyclic hydrocarbon group having 4-20 carbon atoms or a derivative thereof.

[0037]

As examples of the linear or branched alkyl group having 1-4 carbon atoms represented by R^7 in the formula (4), a methyl

group, ethyl group, n-propyl group, isopropyl group, n-butyl group, 2-methylpropyl group, 1-methylpropyl group, t-butyl group, and the like can be given.

Of these alkyl groups, methyl groups, ethyl groups, and the like are particularly preferable.

[0038]

As examples of the monovalent alicyclic hydrocarbon group having 4-20 carbon atoms and the divalent alicyclic hydrocarbon group having 4-20 carbon atoms formed by any two R⁷'s in combination, alicyclic groups derived from a cycloalkane such as norbornane, tricyclodecane, tetracyclododecane, adamantane, cyclobutane, cyclopentane, cyclohexane, cycloheptane, or cyclooctane, and groups obtained by replacing hydrogen atoms on these alicyclic groups with one or more linear or branched alkyl groups having 1-4 carbon atoms, such as methyl group, ethyl group, n-propyl group, isopropyl group, n-butyl group, 2-methylpropyl group, 1-methylpropyl group, or t-butyl group, can be given.

Of these monovalent and divalent alicyclic hydrocarbon groups, groups containing an alicyclic ring derived from norbornane, tricyclodecane, tetracyclododecane, or adamantane, and groups in which hydrogen atoms on these alicyclic ring-containing groups are substituted with the above alkyl groups are preferable.

[0039]

As examples of derivatives of the monovalent or divalent alicyclic hydrocarbon groups, groups having one or more

substituents such as a hydroxyl group; a carboxyl group; a linear or branched hydroxyalkyl group having 1-4 carbon atoms such as a hydroxymethyl group, 1-hydroxyethyl group, 2-hydroxyethyl group, 1-hydroxy-n-propyl group, 2-hydroxy-n-propyl group, 3-hydroxy-n-propyl group, 1-hydroxy-n-butyl group, 2-hydroxy-n-butyl group, 3-hydroxy-n-butyl group, and 4-hydroxy-n-butyl group; a linear or branched alkoxyl group having 1-4 carbon atoms such as a methoxy group, ethoxy group, n-propoxy group, i-propoxy group, n-butoxy group, 2-methylpropoxy group, 1-methylpropoxy group, and t-butoxy group; a cyano group; a linear or branched cyanoalkyl group having 2-5 carbon atoms such as a cyanomethyl group, 1-cyanoethyl group, 2-cyanoethyl group, 1-cyanopropyl group, 2-cyanopropyl group, 3-cyanopropyl group, 1-cyanobutyl group, 2-cyanobutyl group, 3-cyanobutyl group, and 4-cyanobutyl group; and the like can be given.

Of these substituents, a hydroxyl group, carboxyl group, hydroxymethyl group, cyano group, cyanomethyl group, and the like are preferable.

[0040]

The group $-\text{COO}-\text{C}(\text{R}^7)_3$ in the recurring unit (III) in the formula (4) dissociates at the carbonyloxy group ($\text{COO}-$) and the group $-\text{C}(\text{R}^7)_3$ in the presence of an acid, and is herein called acid-dissociating group (ii).

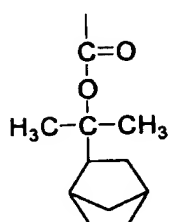
[0041]

Specific preferable examples of the acid-dissociating group (ii) include a t-butoxycarbonyl group and the groups shown

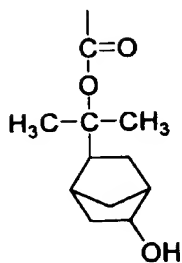
by the following formulas (ii-1) to (ii-57).

[0042]

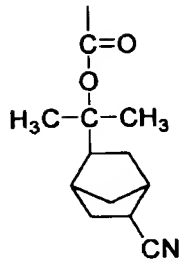
[Formula 15]



(ii-1)



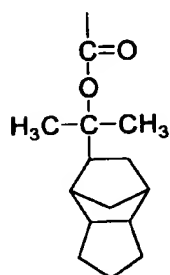
(ii-2)



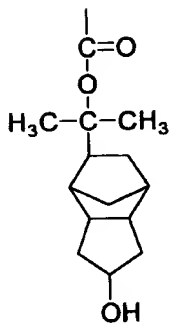
(ii-3)

[0043]

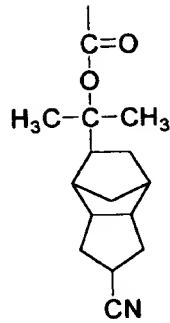
[Formula 16]



(ii-4)



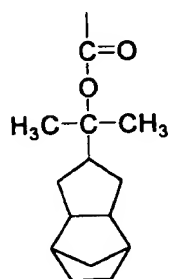
(ii-5)



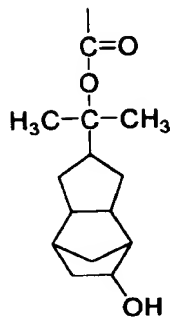
(ii-6)

[0044]

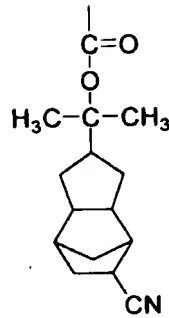
[Formula 17]



(ii-7)



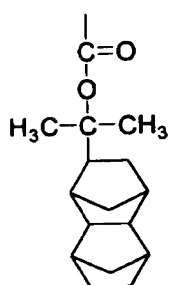
(ii-8)



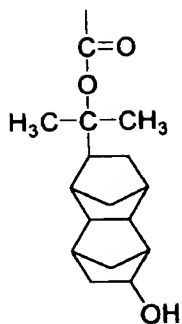
(ii-9)

[0045]

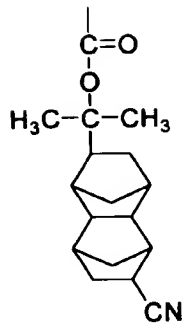
[Formula 18]



(ii-10)



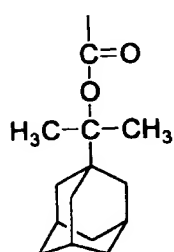
(ii-11)



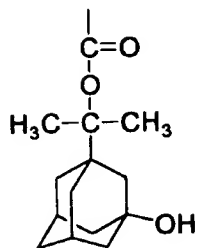
(ii-12)

[0046]

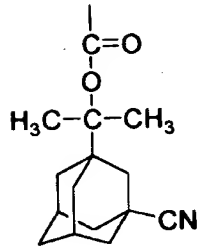
[Formula 19]



(ii-13)



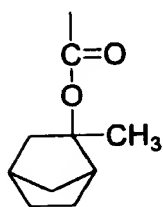
(ii-14)



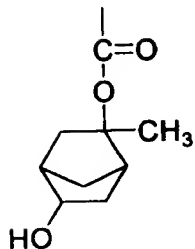
(ii-15)

[0047]

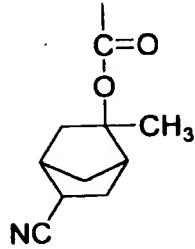
[Formula 20]



(ii-16)



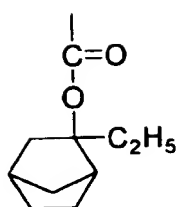
(ii-17)



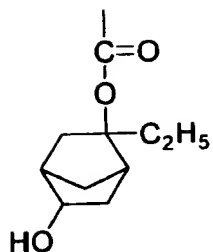
(ii-18)

[0048]

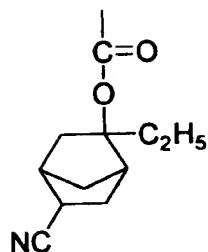
[Formula 21]



(ii-19)



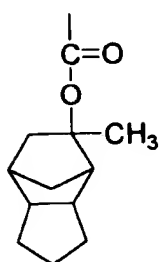
(ii-20)



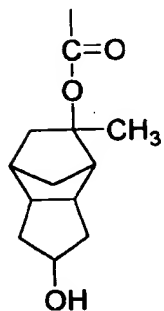
(ii-21)

[0049]

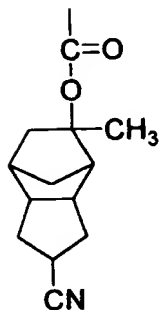
[Formula 22]



(ii-22)



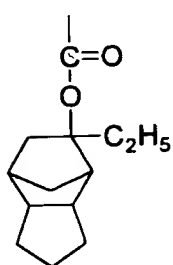
(ii-23)



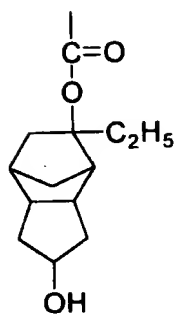
(ii-24)

[0050]

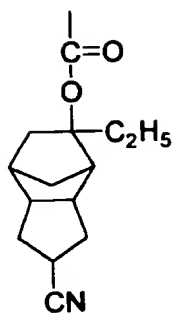
[Formula 23]



(ii-25)



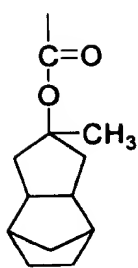
(ii-26)



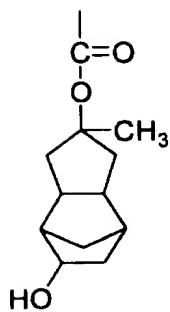
(ii-27)

[0051]

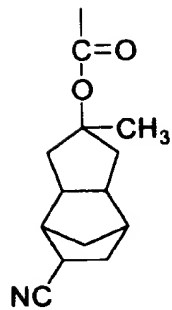
[Formula 24]



(ii-28)



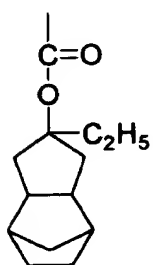
(ii-29)



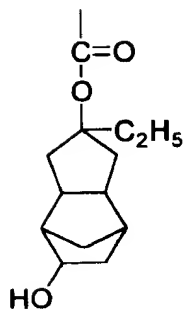
(ii-30)

[0052]

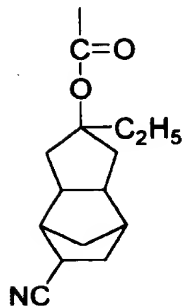
[Formula 25]



(ii-31)



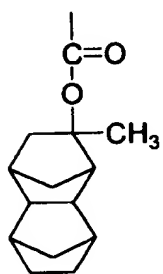
(ii-32)



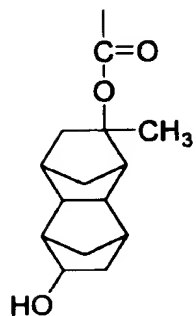
(ii-33)

[0053]

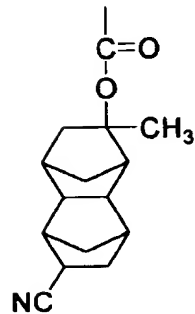
[Formula 26]



(ii-34)



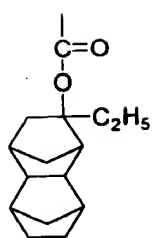
(ii-35)



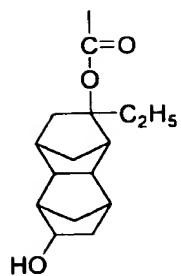
(ii-36)

[0054]

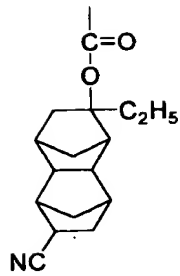
[Formula 27]



(ii-37)



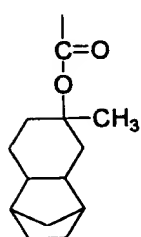
(ii-38)



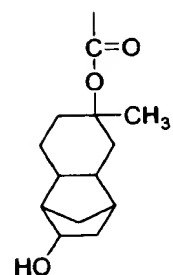
(ii-39)

[0055]

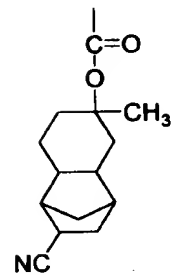
[Formula 28]



(ii-40)



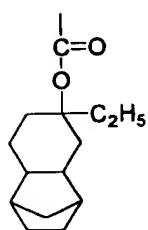
(ii-41)



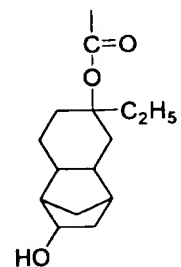
(ii-42)

[0056]

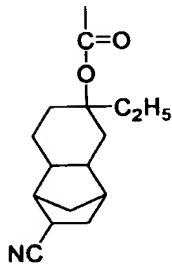
[Formula 29]



(ii-43)



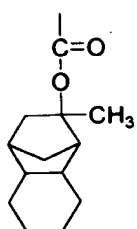
(ii-44)



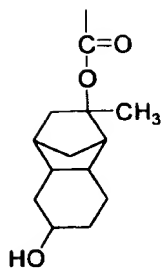
(ii-45)

[0057]

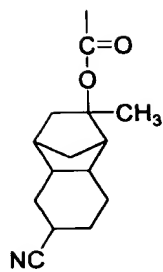
[Formula 30]



(ii-46)



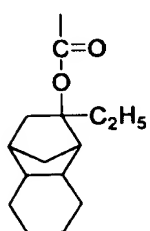
(ii-47)



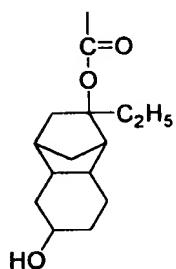
(ii-48)

[0058]

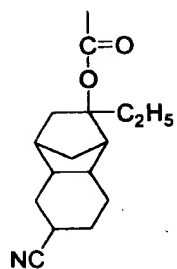
[Formula 31]



(ii-49)



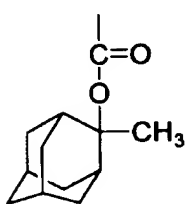
(ii-50)



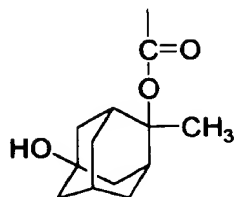
(ii-51)

[0059]

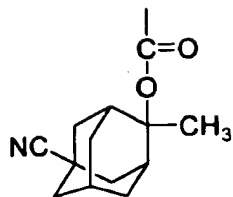
[Formula 32]



(ii-52)



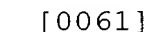
(ii-53)



(ii-54)

[0060]

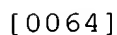
[Formula 33]



[0062]

[0063]

(6)



wherein R^1 , X^1 , and R^2 are the same as defined for the above formula (1), and R^3 , R^4 , R^5 , n , and m have the same meanings as defined for the corresponding symbols in the formula (2).

[0065]

The following compounds can be given as examples of the norbornene derivatives ($\alpha 1$) having $n=m=0$ in the formula (6):

5-(2,2,2-trifluoro-1-hydroxyethyl)bicyclo[2.2.1]hept-2-ene,

5-(2,2,2-trifluoro-1-methyl-1-hydroxyethyl)bicyclo[2.2.1]
hept-2-ene,

5-(2,2,2-trifluoro-1-trifluoromethyl-1-hydroxyethyl)
bicyclo[2.2.1]hept-2-ene,

5-(2,2,2-trifluoro-1-methoxyethyl)bicyclo[2.2.1]hept-2-ene,

5-(2,2,2-trifluoro-1-methyl-1-methoxyethyl)bicyclo[2.2.1]
hept-2-ene,

5-(2,2,2-trifluoro-1-trifluoromethyl-1-methoxyethyl)
bicyclo[2.2.1]hept-2-ene,

5-(2,2,2-trifluoro-1-methylcarbonyloxyethyl)bicyclo[2.2.1]
hept-2-ene,

5-(2,2,2-trifluoro-1-methyl-1-methylcarbonyloxyethyl)
bicyclo[2.2.1]hept-2-ene,

5-(2,2,2-trifluoro-1-trifluoromethyl-1-
methylcarbonyloxyethyl)bicyclo[2.2.1]hept-2-ene,

5-(2,2,2-trifluoro-1-t-butoxycarbonyloxyethyl)bicyclo
[2.2.1]hept-2-ene,

5-(2,2,2-trifluoro-1-methyl-1-t-butoxycarbonyloxyethyl)
bicyclo[2.2.1]hept-2-ene,

5-(2,2,2-trifluoro-1-trifluoromethyl-1-t-

butoxycarbonyloxyethyl)bicyclo[2.2.1]hept-2-ene, and the like.

[0066]

The following compounds can be given as specific examples of norbornene derivatives ($\alpha 1$) having $n=0$ and $m=1$:

5-(2-trifluoromethyl-2-hydroxyethyl)bicyclo[2.2.1]hept-2-ene,

5-(2-trifluoromethyl-2-methyl-2-hydroxyethyl)bicyclo[2.2.1]hept-2-ene,

5-[2,2-bis(trifluoromethyl)-2-hydroxyethyl]bicyclo[2.2.1]hept-2-ene,

5-(2-trifluoromethyl-2-methoxyethyl)bicyclo[2.2.1]hept-2-ene,

5-(2-trifluoromethyl-2-methyl-2-methoxyethyl)bicyclo[2.2.1]hept-2-ene,

5-[2,2-bis(trifluoromethyl)-2-methoxyethyl]bicyclo[2.2.1]hept-2-ene,

5-[2-trifluoromethyl-2-methylcarbonyloxyethyl]bicyclo[2.2.1]hept-2-ene,

5-(2-trifluoromethyl-2-methyl-2-methylcarbonyloxyethyl)bicyclo[2.2.1]hept-2-ene,

5-[2,2-bis(trifluoromethyl)-2-methylcarbonyloxyethyl]bicyclo[2.2.1]hept-2-ene,

5-[2-trifluoromethyl-2-t-butoxycarbonyloxyethyl]bicyclo[2.2.1]hept-2-ene,

5-(2-trifluoromethyl-2-methyl-2-t-butoxycarbonyloxyethyl)bicyclo[2.2.1]hept-2-ene,

5-[2,2-bis(trifluoromethyl)-2-t-butoxycarbonyloxyethyl]
bicyclo[2.2.1]hept-2-ene, and the like.

[0067]

The following compounds can be given as examples of the
norbornene derivatives ($\alpha 1$) having $n=1$ and $m=0$ in the formula
(6):

8-(2,2,2-trifluoro-1-hydroxyethyl)tetracyclo
[4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene,
8-(2,2,2-trifluoro-1-methyl-1-hydroxyethyl)tetracyclo
[4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene,
8-(2,2,2-trifluoro-1-trifluoromethyl-1-hydroxyethyl)
tetracyclo[4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene,
8-(2,2,2-trifluoro-1-methoxyethyl)tetracyclo
[4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene,
8-(2,2,2-trifluoro-1-methyl-1-methoxyethyl)tetracyclo
[4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene,
8-(2,2,2-trifluoro-1-trifluoromethyl-1-methoxyethyl)
tetracyclo[4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene,
8-(2,2,2-trifluoro-1-methylcarbonyloxyethyl)tetracyclo
[4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene,
8-(2,2,2-trifluoro-1-methyl-1-methylcarbonyloxyethyl)
tetracyclo[4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene,
8-(2,2,2-trifluoro-1-trifluoromethyl-1-methylcarbonyloxy
ethyl)tetracyclo[4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene,
8-(2,2,2-trifluoro-1-t-butoxycarbonyloxyethyl)tetracyclo
[4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene,
8-(2,2,2-trifluoro-1-methyl-1-t-butoxycarbonyloxyethyl)

tetracyclo[4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene,
8-(2,2,2-trifluoro-1-trifluoromethyl-1-t-
butoxycarbonyloxyethyl)tetracyclo[4.4.0.1^{2,5}.1^{7,10}]
dodec-3-ene, and the like.

[0068]

The following compounds can be given as examples of the
norbornene derivatives ($\alpha 1$) having $n=1$ and $m=1$:

8-(2-trifluoromethyl-2-hydroxyethyl)tetracyclo
[4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene,
8-(2-trifluoromethyl-2-methyl-2-hydroxyethyl)tetracyclo
[4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene,
8-[2,2-bis(trifluoromethyl)-2-hydroxyethyl]tetracyclo
[4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene,
8-(2-trifluoromethyl-2-methoxyethyl)tetracyclo
[4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene,
8-(2-trifluoromethyl-2-methyl-2-methoxyethyl)tetracyclo
[4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene,
8-[2,2-bis(trifluoromethyl)-2-methoxyethyl]tetracyclo
[4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene,
8-[2-trifluoromethyl-2-methylcarbonyloxyethyl]tetracyclo
[4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene,
8-(2-trifluoromethyl-2-methyl-2-methylcarbonyloxyethyl)
tetracyclo[4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene,
8-[2,2-bis(trifluoromethyl)-2-methylcarbonyloxyethyl]
tetracyclo[4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene,
8-[2-trifluoromethyl-2-t-butoxycarbonyloxyethyl]
tetracyclo[4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene,

8-(2-trifluoromethyl-2-methyl-2-t-butoxycarbonyloxyethyl)
tetracyclo[4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene,
8-[2,2-bis(trifluoromethyl)-2-t-butoxycarbonyloxyethyl]
tetracyclo[4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene, and the like.

[0069]

Of these norbornene derivatives (α 1), the following
compounds are preferable:

5-(2,2,2-trifluoro-1-trifluoromethyl-1-hydroxyethyl)
bicyclo[2.2.1]hept-2-ene,
5-(2,2,2-trifluoro-1-trifluoromethyl-1-methoxyethyl)
bicyclo[2.2.1]hept-2-ene,
5-(2,2,2-trifluoro-1-trifluoromethyl-1-
methylcarbonyloxyethyl)bicyclo[2.2.1]hept-2-ene,
5-(2,2,2-trifluoro-1-trifluoromethyl-1-t-
butoxycarbonyloxyethyl)bicyclo[2.2.1]hept-2-ene,
5-[2,2-bis(trifluoromethyl)-2-hydroxyethyl]bicyclo[2.2.1]
hept-2-ene,
5-[2,2-bis(trifluoromethyl)-2-methoxyethyl]bicyclo[2.2.1]
hept-2-ene,
5-[2,2-bis(trifluoromethyl)-2-methylcarbonyloxyethyl]
bicyclo[2.2.1]hept-2-ene,
5-[2,2-bis(trifluoromethyl)-2-t-butoxycarbonyloxyethyl]
bicyclo[2.2.1]hept-2-ene,

[0070]

8-(2,2,2-trifluoro-1-trifluoromethyl-1-hydroxyethyl)
tetracyclo[4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene,
8-(2,2,2-trifluoro-1-trifluoromethyl-1-methoxyethyl)

tetracyclo[4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene,
 8-(2,2,2-trifluoro-1-trifluoromethyl-1-methylcarbonyloxyethyl)tetracyclo[4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene, 8-(2,2,2-trifluoro-1-trifluoromethyl-1-t-butoxycarbonyloxyethyl)tetracyclo[4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene, 8-[2,2-bis(trifluoromethyl)-2-hydroxyethyl]tetracyclo[4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene, 8-[2,2-bis(trifluoromethyl)-2-methoxyethyl]tetracyclo[4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene, 8-[2,2-bis(trifluoromethyl)-2-methylcarbonyloxyethyl]tetracyclo[4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene, 8-[2,2-bis(trifluoromethyl)-2-t-butoxycarbonyloxyethyl]tetracyclo[4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene, and the like.

The norbornene derivatives (α 1) can be synthesized by the method disclosed by Hiroshi Ito et al. in The American Chemical Society Symposium (1998) (see Preprint, pages 208-211).

[0071]

The monomer providing the recurring unit (II) in the resin (A1-1) and resin (A1-2) is maleic anhydride. Maleic anhydride copolymerizes well with norbornene derivatives (α 1), later described norbornenes and norbornene derivatives (β -1), and other norbornene derivatives. The copolymerization with maleic anhydride increases the molecular weight of the resulting resin (A1-1) and resin (A1-2) to a desired level.

The monomer providing the recurring unit (III) in the resin (A1-2) is a compound derived from (meth)acrylic acid by

The recurring unit (III) may be present in the resin (A1-2) either individually or in combination of two or more.

The resin (A1), resin (A1-1), and resin (A1-2) may comprise at least one recurring unit other than the recurring units (I), (II), or (III) (hereinafter referred to as "other recurring units (a)").

[0073]

$$\begin{array}{c} \text{---(HC---CH)---} \\ | \\ \diagdown \quad / \\ | \quad | \\ \diagup \quad \diagdown \\ | \quad | \\ \diagdown \quad / \\ | \quad | \\ \diagup \quad \diagdown \\ | \quad | \\ \diagdown \quad / \\ | \quad | \\ \diagup \quad \diagdown \\ | \quad | \\ \text{A X Y B} \end{array} \quad (7)$$

44

having 1-4 carbon atoms, and i is an integer of 0 to 2.

[0074]

In addition to the above acid-dissociating group (ii), the following groups can be given as examples of the acid-dissociating group represented by A or B in the formula (7): a linear, branched, or cyclic alkoxy carbonyl group such as a methoxy carbonyl group, ethoxy carbonyl group, n-propoxy carbonyl group, i-propoxy carbonyl group, n-butoxy carbonyl group, 2-methylpropoxy carbonyl group, 1-methylpropoxy carbonyl group, n-pentyloxy carbonyl group, n-hexyloxy carbonyl group, n-heptyloxy carbonyl group, n-octyloxy carbonyl group, n-decyloxy carbonyl group, cyclopentyloxy carbonyl group, cyclohexyloxy carbonyl group, 4-t-butylcyclohexyloxy carbonyl group, cycloheptyloxy carbonyl group, and cyclooctyloxy carbonyl group; an aryloxy carbonyl group such as a phenoxy carbonyl group, 4-t-butylphenoxy carbonyl group, and 1-naphthyloxy carbonyl group; an aralkyloxy carbonyl group such as a benzyloxy carbonyl group, 4-t-butylbenzyloxy carbonyl group, phenethyloxy carbonyl group, and 4-t-butylphenethyloxy carbonyl group;

[0075]

a linear, branched, or cyclic 1-alkyloxyethoxy carbonyl group such as a 1-methoxyethoxy carbonyl group, 1-ethoxyethoxy carbonyl group, 1-n-propoxyethoxy carbonyl group, 1-i-propoxyethoxy carbonyl group, 1-n-butoxyethoxy carbonyl group,

1-(2'-methylpropoxy)ethoxycarbonyl group,
 1-(1'-methylpropoxy)ethoxycarbonyl group,
 1-t-butoxyethoxycarbonyl group,
 1-cyclohexyloxyethoxycarbonyl group, and
 1-(4'-t-butylcyclohexyloxy)ethoxycarbonyl group;
 a 1-aryloxyethoxycarbonyl group such as a
 1-phenoxyethoxycarbonyl group,
 1-(4'-t-butylphenoxy)ethoxycarbonyl group, and
 1-(1'-naphthyloxy)ethoxycarbonyl group;
 a 1-aralkyloxyethoxycarbonyl group such as a
 1-benzyloxyethoxycarbonyl group,
 1-(4'-t-butylbenzyloxy)ethoxycarbonyl group,
 1-phenethyloxyethoxycarbonyl group, and
 1-(4'-t-butylphenethyloxy)ethoxycarbonyl group;

[0076]

a linear, branched, or cyclic alkoxycarbonylmethoxycarbonyl
 group such as a methoxycarbonylmethoxycarbonyl group,
 ethoxycarbonylmethoxycarbonyl group,
 n-propoxycarbonylmethoxycarbonyl group,
 i-propoxycarbonylmethoxycarbonyl group,
 n-butoxycarbonylmethoxycarbonyl group,
 2-methylpropoxycarbonylmethoxycarbonyl group,
 1-methylpropoxycarbonylmethoxycarbonyl group,
 t-butoxycarbonylmethoxycarbonyl group,
 cyclohexyloxy carbonylmethoxycarbonyl group, and
 4-t-butylcyclohexyloxy carbonylmethoxycarbonyl group;
 a linear, branched, or cyclic alkoxycarbonylmethyl group such

as a methoxycarbonylmethyl group, ethoxycarbonylmethyl group, n-propoxycarbonylmethyl group, i-propoxycarbonylmethyl group, n-butoxycarbonylmethyl group, 2-methylpropoxycarbonylmethyl group, 1-methylpropoxycarbonylmethyl group, t-butoxycarbonylmethyl group, cyclohexyloxycarbonylmethyl group, and 4-t-butylcyclohexyloxycarbonylmethyl group; an aryloxycarbonylmethyl group such as a phenoxycarbonylmethyl group, 4-t-butylphenoxycarbonylmethyl group, and 1-naphthyloxycarbonylmethyl group; an aralkyloxycarbonylmethyl group such as a benzyloxycarbonylmethyl group, 4-t-butylbenzyloxycarbonylmethyl group, phenethyloxycarbonylmethyl group, and 4-t-butylphenethyloxycarbonylmethyl group;

[0077]

a linear, branched, or cyclic 2-alkoxycarbonylethyl group such as a 2-methoxycarbonylethyl group, 2-ethoxycarbonylethyl group, 2-n-propoxycarbonylethyl group, 2-i-propoxycarbonylethyl group, 2-n-butoxycarbonylethyl group, 2-(2'-methylpropoxy)carbonylethyl group, 2-(1'-methylpropoxy)carbonylethyl group, 2-t-butoxycarbonylethyl group, 2-cyclohexyloxycarbonylethyl group, and 2-(4'-t-butylcyclohexyloxycarbonyl)ethyl group; a 2-aryloxycarbonylethyl group such as a 2-phenoxycarbonylethyl group, 2-(4'-t-butylphenoxycarbonyl)ethyl group, and 2-(1'-naphthyloxycarbonyl)ethyl group;

a 2-aralkyloxycarbonylethyl group such as a 2-benzyloxycarbonylethyl group, 2-(4'-t-butylbenzyloxycarbonyl)ethyl group, 2-phenethyloxycarbonylethyl group, and 2-(4'-t-butylphenethyloxycarbonyl)ethyl group; a tetrahydrofuranyloxycarbonyl group; a tetrahydropyranyloxycarbonyl group; and the like.

[0078]

Of these acid-dissociating groups (iii), t-butoxycarbonyl group and the groups shown by the formulas (ii-1), (ii-2), (ii-10), (ii-11), (ii-13), (ii-14), (ii-16), (ii-17), (ii-22), (ii-23), (ii-34), (ii-35), (ii-40), (ii-41), (ii-52), and (ii-53) are particularly preferable.

In addition to these groups, groups corresponding to the formula -COOR' (wherein R' represents a linear, branched, or cyclic alkyl group having 1-19 carbon atoms) or the formula $\text{-COOCH}_2\text{COOR''}$ (wherein R'' represents a linear, branched, or cyclic alkyl group having 1-17 carbon atoms) are preferable.

[0079]

As examples of linear or branched alkyl groups having 1-4 carbon atoms represented by X or Y, a methyl group, ethyl group, n-propyl group, i-propyl group, n-butyl group, i-butyl group, sec-butyl group, t-butyl group, and the like can be given.

Of these alkyl groups, a methyl group and ethyl group are particularly preferable.

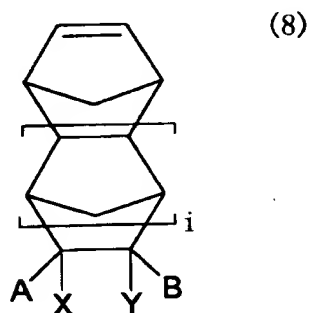
i in the formula (5) is preferably either 0 or 1.

[0080]

As examples of monomers providing the recurring unit (7), compounds shown by the following formula (8) (hereinafter referred to as "norbornene derivatives (β -1)") can be given.

[0081]

[Formula 36]



wherein A, B, X, Y, and i have the same meanings as defined for the formula (7).

[0082]

Given as examples of the norbornene derivatives (β -1) are a compound of the formula (8), wherein either one of A and B, or both, are the acid-dissociating group (ii), the remainder of the A and B, X, and Y are a hydrogen atom, and i is 0; a compound of the formula (8), wherein either one of A and B, or both, are the acid-dissociating group (ii), the remainder of the A and B, X, and Y are a hydrogen atom, and i is 1; and the following compounds:

5-methoxycarbonylbicyclo[2.2.1]hept-2-ene,

5-ethoxycarbonylbicyclo[2.2.1]hept-2-ene,

5-n-propoxycarbonylbicyclo[2.2.1]hept-2-ene,

5-i-propoxycarbonylbicyclo[2.2.1]hept-2-ene,

5-n-butoxycarbonylbicyclo[2.2.1]hept-2-ene,
 5-(2'-methylpropoxy) carbonylbicyclo[2.2.1]hept-2-ene,
 5-(1'-methylpropoxy) carbonylbicyclo[2.2.1]hept-2-ene,
 5-cyclohexyloxy carbonylbicyclo[2.2.1]hept-2-ene,
 5-(4'-t-butylcyclohexyloxy) carbonylbicyclo[2.2.1]hept-2-ene,
 5-phenoxy carbonylbicyclo[2.2.1]hept-2-ene,
 5-(1'-ethoxyethoxy) carbonylbicyclo[2.2.1]hept-2-ene,
 5-(1'-cyclohexyloxyethoxy) carbonylbicyclo[2.2.1]hept-2-ene,
 5-t-butoxycarbonylmethoxycarbonylbicyclo[2.2.1]hept-2-ene,
 5-tetrahydrofuranyloxy carbonylbicyclo[2.2.1]hept-2-ene,
 5-tetrahydropyranyloxy carbonylbicyclo[2.2.1]hept-2-ene,

[0083]

5-methyl-5-methoxycarbonylbicyclo[2.2.1]hept-2-ene,
 5-methyl-5-ethoxycarbonylbicyclo[2.2.1]hept-2-ene,
 5-methyl-5-n-propoxycarbonylbicyclo[2.2.1]hept-2-ene,
 5-methyl-5-i-propoxycarbonylbicyclo[2.2.1]hept-2-ene,
 5-methyl-5-n-butoxycarbonylbicyclo[2.2.1]hept-2-ene,
 5-methyl-5-(2'-methylpropoxy) carbonylbicyclo[2.2.1]hept-2-ene,
 5-methyl-5-(1'-methylpropoxy) carbonylbicyclo[2.2.1]hept-2-ene,
 5-methyl-5-t-butoxycarbonylbicyclo[2.2.1]hept-2-ene,
 5-methyl-5-cyclohexyloxy carbonylbicyclo[2.2.1]hept-2-ene,
 5-methyl-5-(4'-t-butylcyclohexyloxy) carbonylbicyclo[2.2.1]hept-2-ene,

5-methyl-5-phenoxy carbonylbicyclo[2.2.1]hept-2-ene,
5-methyl-5-(1'-ethoxyethoxy) carbonylbicyclo[2.2.1]hept-2-ene,
5-methyl-5-(1'-cyclohexyloxyethoxy) carbonylbicyclo[2.2.1]hept-2-ene,
5-methyl-5-t-butoxycarbonylmethoxycarbonylbicyclo[2.2.1]hept-2-ene,
5-methyl-5-tetrahydrofuranyloxycarbonylbicyclo[2.2.1]hept-2-ene,
5-methyl-5-tetrahydropyranyloxycarbonylbicyclo[2.2.1]hept-2-ene,

[0084]

5,6-di(methoxycarbonyl)bicyclo[2.2.1]hept-2-ene,
5,6-di(ethoxycarbonyl)bicyclo[2.2.1]hept-2-ene,
5,6-di(n-propoxycarbonyl)bicyclo[2.2.1]hept-2-ene,
5,6-di(i-propoxycarbonyl)bicyclo[2.2.1]hept-2-ene,
5,6-di(n-butoxycarbonyl)bicyclo[2.2.1]hept-2-ene,
5,6-di(2'-methylpropoxycarbonyl)bicyclo[2.2.1]hept-2-ene,
5,6-di(1'-methylpropoxycarbonyl)bicyclo[2.2.1]hept-2-ene,
5,6-di(t-butoxycarbonyl)bicyclo[2.2.1]hept-2-ene,
5,6-di(cyclohexyloxycarbonyl)bicyclo[2.2.1]hept-2-ene,
5,6-di(4'-t-butylcyclohexyloxycarbonyl)bicyclo[2.2.1]hept-2-ene,
5,6-di(phenoxy carbonyl)bicyclo[2.2.1]hept-2-ene,
5,6-di(1'-ethoxyethoxycarbonyl)bicyclo[2.2.1]hept-2-ene,
5,6-di(1'-cyclohexyloxyethoxycarbonyl)bicyclo[2.2.1]hept-2-ene,

5,6-di(t-butoxycarbonylmethoxycarbonyl)bicyclo[2.2.1]hept-
2-ene, ✓

5,6-di(tetrahydrofuranyloxycarbonyl)bicyclo[2.2.1]hept-
2-ene,

5,6-di(tetrahydropyranyloxycarbonyl)bicyclo[2.2.1]hept-
2-ene,

[0085]

8-methoxycarbonyltetracyclo[4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene,

8-ethoxycarbonyltetracyclo[4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene,

8-n-propoxycarbonyltetracyclo[4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene,

8-i-propoxycarbonyltetracyclo[4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene,

8-n-butoxycarbonyltetracyclo[4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene,

8-(2'-methylpropoxy)carbonyltetracyclo[4.4.0.1^{2,5}.1^{7,10}]-
dodec-3-ene,

8-(1'-methylpropoxy)carbonyltetracyclo[4.4.0.1^{2,5}.1^{7,10}]-
dodec-3-ene,

8-t-butoxycarbonyltetracyclo[4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene,

8-cyclohexyloxycarbonyltetracyclo[4.4.0.1^{2,5}.1^{7,10}]dodec-3-
ene,

8-(4'-t-butylcyclohexyloxy)carbonyltetracyclo-
[4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene,

8-phenoxy carbonyltetracyclo[4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene,

8-(1'-ethoxyethoxy)carbonyltetracyclo[4.4.0.1^{2,5}.1^{7,10}]-
dodec-3-ene,

8-(1'-cyclohexyloxyethoxy)carbonyltetracyclo-
[4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene,

8-t-butoxycarbonylmethoxycarbonyltetracyclo-

[4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene,
 8-tetrahydrofuranyloxycarbonyltetracyclo[4.4.0.1^{2,5}.1^{7,10}]-
 dodec-3-ene,
 8-tetrahydropyranyloxycarbonyltetracyclo[4.4.0.1^{2,5}.1^{7,10}]-
 dodec-3-ene,
 [0086]
 8-methyl-8-methoxycarbonyltetracyclo[4.4.0.1^{2,5}.1^{7,10}]dodec-
 3-ene,
 8-methyl-8-ethoxycarbonyltetracyclo[4.4.0.1^{2,5}.1^{7,10}]dodec-
 3-ene,
 8-methyl-8-n-propoxycarbonyltetracyclo[4.4.0.1^{2,5}.1^{7,10}]-
 dodec-3-ene,
 8-methyl-8-i-propoxycarbonyltetracyclo[4.4.0.1^{2,5}.1^{7,10}]-
 dodec-3-ene,
 8-methyl-8-n-butoxycarbonyltetracyclo[4.4.0.1^{2,5}.1^{7,10}]-
 dodec-3-ene,
 8-methyl-8-(2'-methylpropoxy)carbonyltetracyclo-
 [4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene,
 8-methyl-8-(1'-methylpropoxy)carbonyltetracyclo-
 [4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene,
 8-methyl-8-t-butoxycarbonyltetracyclo[4.4.0.1^{2,5}.1^{7,10}]-✓
 dodec-3-ene,
 8-methyl-8-cyclohexyloxycarbonyltetracyclo[4.4.0.1^{2,5}.1^{7,10}]-
 dodec-3-ene, /
 8-methyl-8-(4'-t-butylcyclohexyloxy)carbonyltetracyclo-✓
 [4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene,
 8-methyl-8-phenoxy carbonyltetracyclo[4.4.0.1^{2,5}.1^{7,10}]dodec-

3-ene,

8-methyl-8-(1'-ethoxyethoxy)carbonyltetracyclo-

[4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene,

8-methyl-8-(1'-cyclohexyloxyethoxy)carbonyltetracyclo-

[4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene,

8-methyl-8-t-butoxycarbonylmethoxycarbonyltetracyclo

[4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene,

8-methyl-8-tetrahydrofuranyloxy carbonyltetracyclo-

[4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene,

8-methyl-8-tetrahydropyranyloxy carbonyltetracyclo-

[4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene,

[0087]

8,9-di(methoxycarbonyl)tetracyclo[4.4.0.1^{2,5}.1^{7,10}]dodec-

3-ene,

8,9-di(ethoxycarbonyl)tetracyclo[4.4.0.1^{2,5}.1^{7,10}]dodec-

3-ene,

8,9-di(n-propoxycarbonyl)tetracyclo[4.4.0.1^{2,5}.1^{7,10}]dodec-

3-ene,

8,9-di(i-propoxycarbonyl)tetracyclo[4.4.0.1^{2,5}.1^{7,10}]dodec-

3-ene,

8,9-di(n-butoxycarbonyl)tetracyclo[4.4.0.1^{2,5}.1^{7,10}]dodec-

3-ene,

8,9-di(2'-methylpropoxycarbonyl)tetracyclo[4.4.0.1^{2,5}.1^{7,10}]-

dodec-3-ene,

8,9-di(1'-methylpropoxycarbonyl)tetracyclo[4.4.0.1^{2,5}.1^{7,10}]-

dodec-3-ene,

8,9-di(t-butoxycarbonyl)tetracyclo[4.4.0.1^{2,5}.1^{7,10}]dodec-

3-ene,
 8,9-di(cyclohexyloxycarbonyl)tetracyclo[4.4.0.1^{2,5}.1^{7,10}]-
 dodec-3-ene,
 8,9-di(4'-t-butylcyclohexyloxycarbonyl)tetracyclo-
 [4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene,
 8,9-di(phenoxy carbonyl)tetracyclo[4.4.0.1^{2,5}.1^{7,10}]dodec-
 3-ene,
 8,9-di(1'-ethoxyethoxycarbonyl)tetracyclo[4.4.0.1^{2,5}.1^{7,10}]-
 dodec-3-ene,
 8,9-di(1'-cyclohexyloxyethoxycarbonyl)tetracyclo-
 [4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene,
 8,9-di(t-butoxycarbonylmethoxycarbonyl)tetracyclo-
 [4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene,
 8,9-di(tetrahydrofuranyloxycarbonyl)tetracyclo-
 [4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene,
 8,9-di(tetrahydropyranyloxycarbonyl)tetracyclo-
 [4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene, and the like.

[0088]

Of these norbornene derivatives (β -1), preferable
 compounds are a compound of the formula (8) in which either one
 of A and B or both are a t-butoxycarbonyl group or the group
 shown by the formulas (ii-1), (ii-2), (ii-10), (ii-11), (ii-13),
 (ii-14), (ii-16), (ii-17), (ii-22), (ii-23), (ii-34), (ii-35),
 (ii-40), (ii-41), (ii-52), and (ii-53), the remainder of the
 A and B, X, and Y are a hydrogen atom, and i is 0;
 a compound of the formula (8) in which either one of A and B
 or both are a t-butoxycarbonyl group or the group shown by the

formulas (ii-1), (ii-2), (ii-10), (ii-11), (ii-13), (ii-14), (ii-16), (ii-17), (ii-22), (ii-23), (ii-34), (ii-35), (ii-40), (ii-41), (ii-52), and (ii-53), the remainder of the A and B, X, and Y are a hydrogen atom, and i is 1; and 5,6-di(t-butoxycarbonylmethoxycarbonyl)bicyclo[2.2.1]hept-2-ene, 8-methyl-8-t-butoxycarbonyltetracyclo[4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene, 8-methyl-8-t-butoxycarbonylmethoxycarbonyltetracyclo[4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene, and the like.

These preferable norbornene derivatives (β -1) may also be used as a monomer which provides the other recurring unit (b) in the resin (A2) described later.

[0089]

The following compounds can be given as examples of monomers which provide the recurring unit (a) other than the recurring unit (7): monofunctional monomers including norbornenes such as norbornene (specifically, bicyclo[2.2.1]hept-2-ene), 5-methylbicyclo[2.2.1]hept-2-ene, 5-ethylbicyclo[2.2.1]hept-2-ene, 5-hydroxybicyclo[2.2.1]hept-2-ene, 5-hydroxymethylbicyclo[2.2.1]hept-2-ene, tetracyclo[4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene, 8-methyltetracyclo[4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene, 8-ethyltetracyclo[4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene, 8-hydroxytetracyclo[4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene, 8-hydroxymethyltetracyclo[4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene,

8-fluorotetracyclo[4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene,
 8-fluoromethyltetracyclo[4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene,
 8-difluoromethyltetracyclo[4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene,
 8-trifluoromethyltetracyclo[4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene,
 8-pentafluoroethyltetracyclo[4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene,
 8,8-difluorotetracyclo[4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene,
 8,9-difluorotetracyclo[4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene,
 8,8-bis(trifluoromethyl)tetracyclo[4.4.0.1^{2,5}.1^{7,10}]dodec-
 3-ene,
 8,9-bis(trifluoromethyl)tetracyclo[4.4.0.1^{2,5}.1^{7,10}]dodec-
 3-ene,
 8-methyl-8-trifluoromethyltetracyclo[4.4.0.1^{2,5}.1^{7,10}]dodec-
 3-ene,
 8,8,9-trifluorotetracyclo[4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene,
 8,8,9-tris(trifluoromethyl)tetracyclo[4.4.0.1^{2,5}.1^{7,10}]-
 dodec-3-ene,

[0090]

8,8,9,9-tetrafluorotetracyclo[4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene,
 8,8,9,9-tetrakis(trifluoromethyl)tetracyclo-
 [4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene,
 8,8-difluoro-9,9-bis(trifluoromethyl)tetracyclo-
 [4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene,
 8,9-difluoro-8,9-bis(trifluoromethyl)tetracyclo-
 [4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene,
 8,8,9-trifluoro-9-trifluoromethyltetracyclo-
 [4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene,
 8,8,9-trifluoro-9-trifluoromethoxytetracyclo-

[4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene,
 8,8,9-trifluoro-9-pentafluoropropoxytetracyclo-
 [4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene,
 8-fluoro-8-pentafluoroethyl-9,9-bis(trifluoromethyl)-
 tetracyclo[4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene,
 8,9-difluoro-8-heptafluoroisopropyl-9-trifluoromethyl-
 tetracyclo[4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene,
 8-chloro-8,9,9-trifluorotetracyclo[4.4.0.1^{2,5}.1^{7,10}]dodec-
 3-ene,
 8,9-dichloro-8,9-bis(trifluoromethyl)tetracyclo-
 [4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene,
 8-(2',2',2'-trifluorocarboethoxy)tetracyclo-
 [4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene, and
 8-methyl-8-(2',2',2'-trifluorocarboethoxy)tetracyclo-
 [4.4.0.1^{2,5}.1^{7,10}]-dodec-3-ene, or derivatives of these
 norbornenes (hereinafter collectively referred to as
 "norbornene compounds (β -2)");

[0091]

other alicyclic unsaturated compounds such as
 dicyclopentadiene, tricyclo[5.2.1.0^{2,6}]deca-8-ene,
 tricyclo[5.2.1.0^{2,6}]dec-3-ene,
 tricyclo[4.4.0.1^{2,5}]undec-3-ene,
 tricyclo[6.2.1.0^{1,8}]undec-9-ene,
 tricyclo[6.2.1.0^{1,8}]undec-4-ene,
 tetracyclo[4.4.0.1^{2,5}.1^{7,10}.0^{1,6}]dodec-3-ene,
 8-methyltetracyclo[4.4.0.1^{2,5}.1^{7,10}.0^{1,6}]dodec-3-ene,
 8-ethylidenetetracyclo[4.4.0.1^{2,5}.1^{7,10}.0^{1,12}]dodec-3-ene,

8-ethylidenetetracyclo[4.4.0.1^{2,5}.1^{7,10}.0^{1,6}]dodec-3-ene,
pentacyclo[6.5.1.1^{3,6}.0^{2,7}.0^{9,13}]pentadec-4-ene, and
pentacyclo[7.4.0.1^{2,5}.1^{9,12}.0^{8,13}]pentadec-3-ene;

[0092]

(meth)acrylates such as methyl (meth)acrylate, ethyl
(meth)acrylate, n-propyl (meth)acrylate, n-butyl
(meth)acrylate, 2-methylpropyl (meth)acrylate,
2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl
(meth)acrylate, 3-hydroxypropyl (meth)acrylate, cyclopropyl
(meth)acrylate, cyclopentyl (meth)acrylate, cyclohexyl
(meth)acrylate, cyclohexenyl (meth)acrylate,
4-methoxycyclohexyl (meth)acrylate,
2-cyclopropyloxycarbonylethyl (meth)acrylate,
2-cyclopentyloxycarbonylethyl (meth)acrylate,
2-cyclohexyloxycarbonylethyl (meth)acrylate,
2-cyclohexenyloxycarbonylethyl (meth)acrylate,
2-(4'-methoxycyclohexyl)oxycarbonylethyl (meth)acrylate,
norbornyl (meth)acrylate, isobornyl (meth)acrylate,
tricyclodecanyl (meth)acrylate, tetracyclodecanyl
(meth)acrylate, dicyclopentenyl (meth)acrylate, adamantyl
(meth)acrylate, adamantylmethyl (meth)acrylate, and
1-methyladamantyl (meth)acrylate;
 α -hydroxymethylacrylic acid esters such as methyl
 α -hydroxymethyl acrylate, ethyl α -hydroxymethyl acrylate,
n-propyl α -hydroxymethyl acrylate, and n-butyl
 α -hydroxymethyl acrylate;

[0093]

(meth) acryloyloxy lactone compound having an acid-dissociating group such as

α -(meth) acryloyloxy- β -methoxycarbonyl- γ -butyrolactone,
 α -(meth) acryloyloxy- β -ethoxycarbonyl- γ -butyrolactone,
 α -(meth) acryloyloxy- β -n-propoxycarbonyl- γ -butyrolactone,
 α -(meth) acryloyloxy- β -i-propoxycarbonyl- γ -butyrolactone,
 α -(meth) acryloyloxy- β -n-butoxycarbonyl- γ -butyrolactone,
 α -(meth) acryloyloxy- β -(2-methylpropoxy) carbonyl- γ -butyrolactone,
 α -(meth) acryloyloxy- β -(1-methylpropoxy) carbonyl- γ -butyrolactone,
 α -(meth) acryloyloxy- β -t-butoxycarbonyl- γ -butyrolactone,
 α -(meth) acryloyloxy- β -cyclohexyloxy carbonyl- γ -butyrolactone,
 α -(meth) acryloyloxy- β -(4-t-butylcyclohexyloxy) carbonyl- γ -butyrolactone,
 α -(meth) acryloyloxy- β -phenoxycarbonyl- γ -butyrolactone,
 α -(meth) acryloyloxy- β -(1-ethoxyethoxy) carbonyl- γ -butyrolactone,
 α -(meth) acryloyloxy- β -(1-cyclohexyloxyethoxy) carbonyl- γ -butyrolactone,
 α -(meth) acryloyloxy- β -t-butoxycarbonylmethoxycarbonyl- γ -butyrolactone,
 α -(meth) acryloyloxy- β -tetrahydrofuranyloxy carbonyl- γ -butyrolactone,
 α -(meth) acryloyloxy- β -tetrahydropyranyloxy carbonyl- γ -butyrolactone,

[0094]

α -methoxycarbonyl- β -(meth)acryloyloxy- γ -butyrolactone,
 α -ethoxycarbonyl- β -(meth)acryloyloxy- γ -butyrolactone,
 α -n-propoxycarbonyl- β -(meth)acryloyloxy- γ -butyrolactone,
 α -i-propoxycarbonyl- β -(meth)acryloyloxy- γ -butyrolactone,
 α -n-butoxycarbonyl- β -(meth)acryloyloxy- γ -butyrolactone,
 α -(2-methylpropoxy)carbonyl- β -(meth)acryloyloxy- γ -
butyrolactone,
 α -(1-methylpropoxy)carbonyl- β -(meth)acryloyloxy- γ -
butyrolactone,
 α -t-butoxycarbonyl- β -(meth)acryloyloxy- γ -butyrolactone,
 α -cyclohexyloxycarbonyl- β -(meth)acryloyloxy- γ -
butyrolactone,
 α -(4-t-butylcyclohexyloxy)carbonyl- β -(meth)acryloyloxy- γ -
butyrolactone,
 α -phenoxycarbonyl- β -(meth)acryloyloxy- γ -butyrolactone,
 α -(1-ethoxyethoxy)carbonyl- β -(meth)acryloyloxy- γ -
butyrolactone,
 α -(1-cyclohexyloxyethoxy)carbonyl- β -(meth)acryloyloxy- γ -
butyrolactone,
 α -t-butoxycarbonylmethoxycarbonyl- β -(meth)acryloyloxy- γ -
butyrolactone,
 α -tetrahydrofuranyloxycarbonyl- β -(meth)acryloyloxy- γ -
butyrolactone, and
 α -tetrahydropyranyloxycarbonyl- β -(meth)acryloyloxy- γ -
butyrolactone;

[0095]

(meth)acryloyloxylactone compound having no acid-dissociating group such as α -(meth)acryloyloxy- γ -butyrolactone, α -(meth)acryloyloxy- β -fluoro- γ -butyrolactone, α -(meth)acryloyloxy- β -hydroxy- γ -butyrolactone, α -(meth)acryloyloxy- β -methyl- γ -butyrolactone, α -(meth)acryloyloxy- β -ethyl- γ -butyrolactone, α -(meth)acryloyloxy- β , β -dimethyl- γ -butyrolactone, α -(meth)acryloyloxy- β -methoxy- γ -butyrolactone, β -(meth)acryloyloxy- γ -butyrolactone, α -fluoro- β -(meth)acryloyloxy- γ -butyrolactone, α -hydroxy- β -(meth)acryloyloxy- γ -butyrolactone, α -methyl- β -(meth)acryloyloxy- γ -butyrolactone, α -ethyl- β -(meth)acryloyloxy- γ -butyrolactone, α , α -dimethyl- β -(meth)acryloyloxy- γ -butyrolactone, α -methoxy- β -(meth)acryloyloxy- γ -butyrolactone, and α -(meth)acryloyloxy- δ -mevalonolactone;

[0096]

vinyl esters such as vinyl acetate, vinyl propionate, and vinyl butyrate;

unsaturated nitrile compounds such as (meth)acrylonitrile, α -chloroacrylonitrile, crotonitrile, maleinitrile, fumaronitrile, mesaconitrile, citraconitrile, and itaconitrile;

unsaturated amide compounds such as (meth)acrylamide, N,N-dimethyl(meth)acrylamide, crotonamide, maleinamide, fumaramide, mesaconamide, citraconamide, and itaconamide; other nitrogen-containing vinyl compounds such as

N-vinyl-ε-caprolactam, N-vinylpyrrolidone, vinylpyridine, and vinylimidazole;

unsaturated carboxylic acids (anhydrides) such as (meth)acrylic acid, crotonic acid, maleic acid, maleic anhydride, fumaric acid, itaconic acid, itaconic anhydride, citraconic acid, citraconic anhydride, and mesaconic acid; carboxyl group-containing esters of unsaturated carboxylic acids such as 2-carboxyethyl (meth)acrylate, 2-carboxypropyl (meth)acrylate, 3-carboxypropyl (meth)acrylate, 4-carboxybutyl (meth)acrylate, 4-carboxycyclohexyl (meth)acrylate, carboxytricyclodecanyl (meth)acrylate, and carboxytetracyclododecanyl (meth)acrylate; and compounds in which a carboxyl group in the above unsaturated carboxylic acids or carboxyl group-containing esters of unsaturated carboxylic acids is converted into the above acid-dissociating organic group (i); and

[0097]

polyfunctional monomers such as methylene glycol di(meth)acrylate, ethylene glycol di(meth)acrylate, propylene glycol di(meth)acrylate, 1,6-hexanediol di(meth)acrylate, 2,5-dimethyl-2,5-hexanediol di(meth)acrylate, 1,8-octanediol di(meth)acrylate, 1,9-nonanediol di(meth)acrylate, 1,4-bis(2-hydroxypropyl)benzene di(meth)acrylate, 1,3-bis(2-hydroxypropyl)benzene di(meth)acrylate, 1,2-adamantanediol di(meth)acrylate, 1,3-adamantanediol di(meth)acrylate, 1,4-adamantanediol di(meth)acrylate, and tricyclodecanyldimethylol di(meth)acrylate.

[0098]

The amount of the recurring unit (I) in the resin (A1) is 1-100 mol%, preferably 1-90 mol%, and still more preferably 5-80 mol% of the total amount of the recurring units. If the amount of the recurring unit (I) is less than 1 mol%, developability of the resulting radiation-sensitive resin composition tends to decrease.

[0099]

The amount of the recurring unit (I) in the resin (A1-1) is usually 1-50 mol%, preferably 1-40 mol%, and still more preferably 5-40 mol% of the total amount of the recurring units. If the amount of the recurring unit (I) is less than 1 mol%, developability of the resulting radiation-sensitive resin composition tends to decrease. If the amount exceeds 50 mol%, on the other hand, resolution as a resist tends to decrease.

The amount of the recurring unit (II) is usually 1-50 mol%, preferably 5-50 mol%, and still more preferably 10-50 mol% of the total amount of the recurring units. If the content of the recurring unit (II) is less than 1 mol%, the rate of copolymerization decreases and the resulting radiation-sensitive resin composition tends to exhibit decreased developability. If the content exceeds 50 mol%, on the other hand, part of maleic anhydride, which is a monomer providing the recurring unit (II), may remain un-reacted in the polymerization reaction for producing the resin (A1-1).

The amount of the other recurring units (a) is usually 40 mol% or less, and preferably 30 mol% or less.

[0100]

The amount of the recurring unit (I) in the resin (A1-2) is usually 1-50 mol%, preferably 5-50 mol%, and still more preferably 5-45 mol% of the total amount of the recurring units. If the amount of the recurring unit (I) is less than 1 mol%, developability of the resulting radiation-sensitive resin composition tends to decrease. If the amount exceeds 50 mol%, on the other hand, resolution as a resist tends to decrease.

The amount of the recurring unit (II) is usually 1-50 mol%, preferably 5-50 mol%, and still more preferably 5-45 mol% of the total amount of the recurring units. If the content of the recurring unit (II) is less than 1 mol%, developability of the resulting radiation-sensitive resin composition tends to decrease. If the content exceeds 50 mol%, resolution as a resist tends to decrease.

The amount of the recurring unit (III) is usually 1-60 mol%, preferably 5-60 mol%, and still more preferably 10-60 mol% of the total amount of the recurring units. If the content of the recurring unit (III) is less than 1 mol%, resolution as a resist tends to decrease. If the content exceeds 60 mol%, undeveloped areas such as scum tends to be produced due to impaired developability of the resulting radiation-sensitive resin composition.

The amount of the other recurring units (a) is usually 40 mol% or less, and preferably 30 mol% or less.

[0101]

The resin (A1) can be prepared by polymerization of the

norbornene derivatives (A1), preferably together with maleic acid anhydride or maleic acid anhydride and a monomer which provides the recurring unit (III), and optionally with monomers which provide the other recurring units (a) in an appropriate solvent using a radical polymerization initiator such as hydroperoxides, dialkyl peroxides, diacyl peroxides, or azo compounds and, as required, in the presence of a chain-transfer agent.

As examples of the solvent used for polymerization of the components, alkanes such as n-pentane, n-hexane, n-heptane, n-octane, n-nonane, and n-decane; cycloalkanes such as cyclohexane, cycloheptane, cyclooctane, decalin, and norbornane; aromatic hydrocarbons such as benzene, toluene, xylene, ethylbenzene, and cumene; halogenated hydrocarbons such as chlorobutanes, bromohexanes, dichloroethanes, hexamethylene dibromide, and chlorobenzene; saturated carboxylic acid esters such as ethyl acetate, n-butyl acetate, i-butyl acetate, and methyl propionate; ethers such as tetrahydrofuran, dimethoxyethanes, and diethoxyethanes; and the like can be given.

These solvents may be used either individually or in combination of two or more.

The polymerization is carried out at a temperature of usually 40-120°C, and preferably 50-90°C for usually 1-48 hours, and preferably 1-24 hours.

[0102]

It is preferable that the resin (A1) of the present

invention contains almost no impurities such as halogens or metals. The smaller the amount of such impurities, the better are the sensitivity, resolution, process stability, pattern shape, or the like as a resist. The resin (A1) can be purified using, for example, a chemical purification method such as washing with water or liquid-liquid extraction or a combination of the chemical purification method and a physical purification method such as ultra-filtration or centrifugation.

[0103]

Next, the resin (A2) will be explained.

As examples of the linear or branched alkyl group having 1-4 carbon atoms represented by R^8 , R^9 , or R^{10} in the formula (5), a methyl group, ethyl group, n-propyl group, i-propyl group, n-butyl group, 2-methylpropyl group, 1-methylpropyl group, t-butyl group, and the like can be given.

As examples of the monovalent oxygen-containing polar group represented by R^8 , R^9 , or R^{10} , a hydroxyl group; carboxyl group; linear or branched hydroxyalkyl groups having 1-4 carbon atoms such as a hydroxymethyl group, 1-hydroxyethyl group, 2-hydroxyethyl group, 1-hydroxy-n-propyl group, 2-hydroxy-n-propyl group, 3-hydroxy-n-propyl group, 1-hydroxy-n-butyl group, 2-hydroxy-n-butyl group, 3-hydroxy-n-butyl group, and 4-hydroxy-n-butyl group; linear or branched alkoxy groups having 1-4 carbon atoms such as a methoxy group, ethoxy group, n-propoxy group, i-propoxy group, n-butoxy group, 2-methylpropoxy group, 1-methylpropoxy group, and t-butoxy group.

Of these oxygen-containing polar groups, a hydroxyl group, carboxyl group, hydroxymethyl group, methoxy group, ethoxy group, and the like are preferable.

[0104]

As examples of the monovalent nitrogen-containing polar group represented by R^8 , R^9 , or R^{10} , a cyano group; linear or branched cyanoalkyl groups having 2-5 carbon atoms such as a cyanomethyl group, 1-cyanoethyl group, 2-cyanoethyl group, 1-cyano-n-propyl group, 2-cyano-n-propyl group, 3-cyano-n-propyl group, 1-cyano-n-butyl group, 2-cyano-n-butyl group, 3-cyano-n-butyl group, and 4-cyano-n-butyl group.

Of these nitrogen-containing polar groups, a cyano group, cyanomethyl group, 1-cyanoethyl group, and the like are preferable.

[0105]

Particularly preferable groups represented by R^8 , R^9 , or R^{10} in the formula (5) are a hydrogen atom, methyl group, ethyl group, hydroxyl group, carboxyl group, hydroxymethyl group, methoxy group, ethoxy group, cyano group, cyanomethyl group, 1-cyanoethyl group, and the like.

m and n in the formula (5) are preferably either 0 or 1.

The structural unit (IV) may be used in the resin (A2) either individually or in combination of two or more.

[0106]

The structural unit (IV) can be formed in the resin (A2)

by the ring-opening polymerization of a compound similar to the norbornene derivative ($\alpha 1$) of the formula (6), but replacing R^3 , R^4 , and R^5 respectively with R^8 , R^9 , and R^{10} (such a compound is hereinafter referred to as "norbornene derivative ($\alpha 2$)"), for example, in the presence of a metathesis catalyst described later.

The resin (A2) may further comprise one or more other structural units obtained by a ring opening polymerization using a metathesis catalyst (hereinafter referred to as "other structural unit (b)").

As examples of monomers which provide the other structural unit (b), the same norbornene derivatives ($\beta-1$), norbornene compounds ($\beta-2$), and other alicyclic unsaturated compounds given in connection with the resin (A1) can be given.

[0107]

The amount of the structural unit (IV) in the resin (A2) is 1-100 mol%, preferably 5-90 mol%, and still more preferably 10-80 mol% of the total amount of the structural units. If the amount of the structural unit (IV) is less than 1 mol%, developability of the resulting radiation-sensitive resin composition tends to decrease.

[0108]

The resin (A2) is prepared by the ring-opening (co)polymerization of a norbornene derivative ($\alpha 2$), optionally together with a norbornene derivative ($\beta-1$), norbornene compound ($\beta-2$), and other monomers such as an alicyclic unsaturated compound which is copolymerizable by the

ring-opening (co)polymerization in an appropriate solvent using a metathesis catalyst.

[0109]

The metathesis catalyst is usually a combination of at least one compound of an element selected from the group consisting of W, Mo, and Re (hereinafter referred to as "specific transition metal compound") and a compound of a metal belonging to the group IA, IIA, IIIA, IVA, or IVB of Deming's Periodic Table and having a metal-carbon bond or metal-hydrogen bond (hereinafter referred to as "specific organometallic compound").

As examples of the specific transition metal compound, a halide, oxyhalide, alkoxyhalide, alkoxide, carbonate, (oxy)acetylacetonate, carbonyl complex, acetonitrile complex, and hydride complex of W, Mo, or Re, derivatives of these compounds, and the like can be given. Of these compounds, a compound of W or Mo, more particularly a halide, oxyhalide, or alkoxyhalide of W or Mo are preferable in view of polymerization activity and practicability.

The specific transition metal compound can be a compound conjugated by a suitable complexing agent such as triphenylphosphine ($\text{P}(\text{C}_6\text{H}_5)_3$), pyridine (NC_5H_5), or the like.

[0110]

The following compounds can be given as specific examples of the specific transition metal compound: WCl_6 , WCl_5 , WCl_4 , WBr_6 , WF_6 , WI_6 , MoCl_5 , MoCl_4 , MoCl_3 , ReCl_3 , WOCl_4 , WOCl_3 , WOBr_3 , MoOCl_3 , MoOBr_3 , ReOCl_3 , ReOBr_3 , $\text{WCl}_2(\text{OC}_2\text{H}_5)_4$, $\text{W}(\text{OC}_2\text{H}_5)_6$, $\text{MoCl}_3(\text{OC}_2\text{H}_5)_2$,

Mo(OC₂H₅)₅, WO₂(acac)₂ (wherein "acac" indicates an acetylacetonate residue), MoO₂(acac)₂, W(OCOR)₅ (wherein "OCOR" indicates a carboxylic acid residue), Mo(OCOR)₅, W(CO)₆, Mo(CO)₆, Re₂(CO)₁₀, WCl₅ · P(C₆H₅)₃, MoCl₅ · P(C₆H₅)₃, ReOBr₃ · P(C₆H₅)₃, WCl₆ · NC₅H₅, W(CO)₅ · P(C₆H₅)₃, W(CO)₃ · (CH₃CN)₃, and the like.

Of these, WCl₆, MoCl₅, WCl₂(OC₂H₅)₄, MoCl₃(OC₂H₅)₂, and the like are preferable.

These specific transition metal compounds may be used either individually or in combinations of two or more.

The specific transition metal compound component which constitutes a metathesis catalyst may be a mixture of two or more compounds forming specific transition metal compound by reacting in the polymerization reaction system.

[0111]

The following compounds can be given as specific examples of the specific organometallic compounds: n-C₄H₉Li, n-C₅H₁₁Na, C₆H₅Na, CH₃MgI, C₂H₅MgBr, CH₃MgBr, n-C₃H₇MgCl, t-C₄H₉MgCl, CH₂=CHCH₂MgCl, (C₂H₅)₂Zn, (C₂H₅)₂Cd, CaZn(C₂H₅)₄, (CH₃)₃B, (C₂H₅)₃B, (n-C₄H₉)₃B, (CH₃)₃Al, (CH₃)₂AlCl, CH₃AlCl₂, (CH₃)₃Al₂Cl₃, (C₂H₅)₃Al, (C₂H₅)₃Al₂Cl₃, (C₂H₅)₂Al · O(C₂H₅)₂, (C₂H₅)₂AlCl, C₂H₅AlCl₂, (C₂H₅)₂AlH, (C₂H₅)₂AlOC₂H₅, (C₂H₅)₂AlCN, LiAl(C₂H₅)₂, (n-C₃H₇)₃Al, (i-C₄H₉)₃Al, (i-C₄H₉)₂AlH, (n-C₆H₁₃)₃Al, (n-C₈H₁₇)₃Al, (C₆H₅)₃Al, (CH₃)₄Ga, (CH₃)₄Sn, (n-C₄H₉)₄Sn, (C₂H₅)₃SnH, LiH, NaH, B₂H₆, NaBH₄, AlH₃, LiAlH₄, TiH₄, and the like.

Of these, (CH₃)₃Al, (CH₃)₂AlCl, CH₃AlCl₂, (CH₃)₃Al₂Cl₃, (C₂H₅)₃Al, (C₂H₅)₂AlCl, C₂H₅AlCl₂, (C₂H₅)₃Al₂Cl₃, (C₂H₅)₂AlH,

$(C_2H_5)_2AlOC_2H_5$, $(C_2H_5)_2AlCN$, $(n-C_3H_7)_3Al$, $(i-C_4H_9)_3Al$, $(i-C_4H_9)_2AlH$, $(n-C_6H_{13})_3Al$, $(n-C_8H_{17})_3Al$, $(C_6H_5)_3Al$, and the like are preferable.

These specific organometallic compounds may be used either individually or in combinations of two or more.

The metal atomic ratio of the specific transition metal compound and specific organometallic compound is from 1:1 to 1:100, preferably from 1:2 to 1:50.

[0112]

One or more activation agents (a) to (i) may be added to the catalyst consisting of a combination of the specific transition metal compound and specific organometallic compound to promote the catalyst activity.

Activation Agent (a): Boron compounds such as B, BF_3 , BCl_3 , $B(O-n-C_4H_9)_3$, $BF_3 \cdot O(CH_3)_2$, $BF_3 \cdot O(C_2H_5)_2$, $BF_3 \cdot O(n-C_4H_9)_2$, $BF_3 \cdot 2C_6H_5OH$, $BF_3 \cdot 2CH_3COOH$, $BF_3 \cdot CO(NH_2)_2$, $BF_3 \cdot N(C_2H_4OH)_3$, $BF_3 \cdot$ piperidine, $BF_3 \cdot NH_2C_2H_5$, B_2O_3 , and H_3BO_3 ; silicon compounds such as $Si(OC_2H_5)_4$ and $Si(Cl)_4$.

Activation Agent (b): Alcohols, hydroperoxides, dialkylperoxides, and diacylperoxides.

Activation Agent (c): Water

Activation Agent (d): Oxygen

Activation Agent (e): Aldehydes, carbonyl compounds such as ketones, and oligomers or polymers of these compounds

Activation Agent (f): Cyclic ethers such as ethylene oxide, epichlorohydrin, and oxetane

Activation Agent (g): amides such as N,N-dimethylformamide and N,N-dimethylacetamide; amines such as aniline, morpholine, and piperidine; and azo compounds such as azobenzene

Activation Agent (h): N-nitroso compounds such as N-nitrosodimethylamine, N-nitrosodiphenylamine

Activation Agent (i): Compounds having a nitrogen-chlorine bond or a sulfur-chlorine bond such as trichloromelamine, N-chlorosuccinimide, and phenylsulphenyl chloride

The ratio of these activation agents and specific transition metal compound cannot be generically specified because the ratio may considerably vary according to the type of the activation agent used. In many cases, the ratio is in the range from 0.005:1 to 10:1, and preferably from 0.05:1 to 3.0:1.

[0113]

Although the molecular weight of the resin (A2) obtained by the ring-opening (co)polymerization can be controlled by changing the reaction conditions such as the type and concentration of the metathesis catalyst, polymerization temperature, the type and amount of the solvent, the monomer concentration, and the like, the molecular weight control by adding a suitable molecular weight modifier to the reaction

system is preferable.

As examples of the molecular weight modifier, α -olefins such as ethylene, propylene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonene, and 1-decene; α,ω -diolefins such as 1,3-butadiene and 1,4-pentadiene; vinyl aromatic compounds such as styrene and α -methylstyrene; acetylenes; and polar allyl compounds such as allyl chloride, allyl acetate, and trimethylallyloxysilane can be given.

These molecular weight modifiers may be used either individually or in combinations of two or more.

The amount of the molecular weight modifiers is usually 0.005-2 mol%, preferably 0.02-1.0 mol%, and still more preferably 0.03-0.7 mol% for 1 mol of all the monomers.

As examples of the solvent used for the ring-opening (co)polymerization, alkanes such as n-pentane, n-hexane, n-heptane, n-octane, n-nonane, and n-decane; cycloalkanes such as cyclohexane, cycloheptane, cyclooctane, decalin, and norbornane; aromatic hydrocarbons such as benzene, toluene, xylene, ethylbenzene, and cumene; halogenated hydrocarbons such as chlorobutane, bromohexane, dichloroethane, hexamethylene dibromide, and chlorobenzene; saturated carboxylic acid esters such as ethyl acetate, n-butyl acetate, i-butyl acetate, and methyl propionate; and the like can be given.

These solvents may be used either individually or in combination of two or more.

[0114]

From the viewpoint of transmittance of radioactive rays, the resin (A2) of the present invention preferably contains as small an amount of carbon-carbon unsaturated bonds as possible. Such a resin (A2) can be prepared by effecting an addition reaction such as a hydrogenation reaction, hydration reaction, halogenation reaction, and halogenation-hydrogenation reaction at an appropriate time during the course of the ring-opening (co)polymerization or after the ring-opening (co)polymerization. A particularly preferable resin (A2) is that obtained by the hydrogenation reaction.

The degree of hydrogenation of the hydrogenated resin (A2) is preferably 70% or more, more preferably 90% or more, and still more preferably 100%.

A catalyst commonly used in the hydrogenation reaction of olefin compounds can be used in the above hydrogenation reaction.

As examples of a heterogeneous system catalyst among such hydrogenation catalysts, a solid catalyst with a noble metal, such as Pd, Pt, Ni, Rh, or Ru, carried on a carrier such as carbon, silica, alumina, or titanium dioxide can be given. These heterogeneous system catalysts may be used either individually or in combinations of two or more.

As examples of a homogeneous system catalyst, a nickel naphthenate/triethylaluminum catalyst, nickel acetylacetonate/triethylaluminum catalyst, cobalt octenate/n-butyl lithium catalyst, titanocene dichloride/diethylaluminum monochloride catalyst, and a

rhodium catalyst such as rhodium acetate, chlorotris(triphenylphosphine) rhodium, and the like can be given. These homogeneous system catalysts may be used either individually or in combinations of two or more.

Of these hydrogenation catalysts, the heterogeneous system catalysts are preferable due to the high reaction activity, ease of catalyst removal after the reaction, and excellent color tone of the resulting resin (A2).

The hydrogenation reaction is carried out under a hydrogen gas pressure from atmospheric pressure to 300 atm, and preferably from 3 to 200 atm, at a temperature of usually 0-200°C, and preferably 20-180°C.

[0115]

Furthermore, the resin (A2) of the present invention should contain as small an amount of impurities as possible. The impurities mainly originate from the catalyst used in the ring-opening (co)polymerization reaction. Impurities to which particular attention should be paid when the resin composition is used as a resist are halogens such as fluorine, chlorine, and bromine, and metals belonging to the group IV, V, VI, VII, or VIII of the Deming's Periodic Table. A preferable resin (A2) should contain halogen impurities of no more than 3 ppm, particularly no more than 2 ppm, and metal impurities of no more than 300 ppb, and particularly no more than 100 ppb. The impurity content less than the above-described limit ensures sensitivity, resolution, and process stability as a resist and increases the yield of semiconductors produced using

the radiation-sensitive resin composition of the present invention.

As the method for reducing impurities in the resin (A2) when the impurities are remaining halogens, (1) a method of washing or extracting (liquid-liquid extraction) the resin solution with purified water, (2) a combination of washing or liquid-liquid extraction with purified water and a physical purification method such as ultra-filtration, centrifugation, and the like, (3) a method of using an alkaline aqueous solution or an acid aqueous solution instead of purified water in the methods (1) or (2), and the like can be given. When the impurities are residual metals, in addition to the methods (1)-(3), (4) a method of treating the resin by oxidation, reduction, ligand exchange, counter-ion exchange, etc. to increase the solubility of the residual metals in solvents or water, then applying the method (1), (2), or (3) can be given.

These treatments for reducing the amount of impurities can be carried out at an appropriate time after the ring-opening (co)polymerization for manufacturing the resin (A2).

[0116]

The resin (A) of the present invention has an acid-dissociating group. Therefore, when the group R^1 in the structure (1) of the resin (A) is a group other than the acid-dissociating group (i), a monomer having an acid-dissociating group must be copolymerized with the norbornene derivatives ($\alpha 1$) or norbornene derivatives ($\alpha 2$), for example. Such a monomer having an acid-dissociating group

may also be used when the group R^1 is an acid-dissociating group (i).

[0117]

The polystyrene-reduced weight average molecular weight (hereinafter referred to as "Mw") of the resin (A) determined by gel permeation chromatography (GPC) is usually 3,000-300,000, preferably 4,000-200,000, and still more preferably 5,000-100,000. If Mw of the resin (A) is less than 3,000, heat resistance as a resist tends to decrease. If Mw exceeds 300,000, developability as a resist tends to decrease.

The ratio of Mw to the polystyrene-reduced number average molecular weight (hereinafter referred to as "Mn") determined by gel permeation chromatography (GPC) (Mw/Mn) of the resin (A) is usually 1-5, and preferably 1-3.

In the present invention, the resin (A) may be used either individually or in combination of two or more.

[0118]

Component (B)

The component (B) of the present invention is a photoacid generator which generates an acid upon exposure (hereinafter referred to as "acid generator (B)").

The acid generator (B) causes an acid-dissociating group in the resin (A) to dissociate by the action of an acid generated upon exposure. As a result, an exposed part of the resist film becomes readily soluble in an alkaline developer, thereby forming a positive-tone resist pattern.

As examples of the acid generator (B), onium salt

compounds, halogen-containing compounds, diazoketone compounds, sulfone compounds, sulfonate compounds, and the like can be given.

Examples of the acid generator (B) are given below.

[0119]

Onium salt compounds:

As examples of onium salt compounds, iodonium salts, sulfonium salts (including tetrahydrothiophenium salts), phosphonium salts, diazonium salts, pyridinium salts, and the like can be given.

The following compounds can be given as specific preferable examples of onium salt compounds:

diphenyliodoniumtrifluoromethanesulfonate,
diphenyliodoniumnonafluoro-n-butanesulfonate,
diphenyliodoniumperfluoro-n-octanesulfonate,
bis(4-t-butylphenyl)iodoniumtrifluoromethanesulfonate,
bis(4-t-butylphenyl)iodoniumnonafluoro-n-butanesulfonate,
bis(4-t-butylphenyl)iodoniumperfluoro-n-octanesulfonate,
triphenylsulfoniumtrifluoromethanesulfonate,
triphenylsulfoniumnonafluoro-n-butanesulfonate,
triphenylsulfoniumperfluoro-n-octanesulfonate,
triphenylsulfonium 10-camphorsulfonate,
cyclohexyl·2-oxocyclohexyl·methylsulfoniumtrifluoro-
methanesulfonate,
dicyclohexyl·2-oxocyclohexylsulfoniumtrifluoro-
methanesulfonate,
2-oxocyclohexyldimethylsulfoniumtrifluoromethanesulfonate,

1-naphthyldimethylsulfoniumtrifluoromethanesulfonate,
1-naphthyldiethylsulfoniumtrifluoromethanesulfonate,
4-cyano-1-naphthyldimethylsulfoniumtrifluoro-
methanesulfonate,
4-nitro-1-naphthyldimethylsulfoniumtrifluoro-
methanesulfonate,
4-methyl-1-naphthyldimethylsulfoniumtrifluoro-
methanesulfonate,
4-cyano-1-naphthyldiethylsulfoniumtrifluoro-
methanesulfonate,
4-nitro-1-naphthyldiethylsulfoniumtrifluoro-
methanesulfonate,
4-methyl-1-naphthyldiethylsulfoniumtrifluoro-
methanesulfonate,
4-hydroxy-1-naphthyldimethylsulfoniumtrifluoro-
methanesulfonate,

[0120]

4-hydroxy-1-naphthyltetrahydrothiopheniumtrifluoro-
methanesulfonate,
4-hydroxy-1-naphthyltetrahydrothiopheniumnonafluoro-
n-butanesulfonate,
4-hydroxy-1-naphthyltetrahydrothiopheniumperfluoro-
n-octanesulfonate,
4-methoxy-1-naphthyltetrahydrothiopheniumtrifluoro-
methanesulfonate,
4-methoxy-1-naphthyltetrahydrothiopheniumnonafluoro-
n-butanesulfonate,

4-methoxy-1-naphthyltetrahydrothiopheniumperfluoro-
n-octanesulfonate,
4-ethoxy-1-naphthyltetrahydrothiopheniumtrifluoro-
methanesulfonate,
4-ethoxy-1-naphthyltetrahydrothiopheniumnonafluoro-
n-butanesulfonate,
4-ethoxy-1-naphthyltetrahydrothiopheniumperfluoro-
n-octanesulfonate,
4-n-butoxy-1-naphthyltetrahydrothiopheniumtrifluoro-
methanesulfonate,
4-n-butoxy-1-naphthyltetrahydrothiopheniumnonafluoro-
n-butanesulfonate,
4-n-butoxy-1-naphthyltetrahydrothiopheniumperfluoro-
n-octanesulfonate,
4-methoxymethoxy-1-naphthyltetrahydrothiopheniumtrifluoro-
methanesulfonate,
4-methoxymethoxy-1-naphthyltetrahydrothiopheniumnonafluoro-
n-butanesulfonate,
4-methoxymethoxy-1-naphthyltetrahydrothiopheniumperfluoro-
n-octanesulfonate,
4-ethoxymethoxy-1-naphthyltetrahydrothiopheniumtrifluoro-
methanesulfonate,
4-ethoxymethoxy-1-naphthyltetrahydrothiopheniumnonafluoro-
n-butanesulfonate,
4-ethoxymethoxy-1-naphthyltetrahydrothiopheniumperfluoro-
n-octanesulfonate,

[0121]

4-(1'-methoxyethoxy)-1-naphthyltetrahydrothiophenium-
trifluoromethanesulfonate,
4-(1'-methoxyethoxy)-1-naphthyltetrahydrothiophenium-
nonafluoro-n-butanesulfonate,
4-(1'-methoxyethoxy)-1-naphthyltetrahydrothiophenium-
perfluoro-n-octanesulfonate,
4-(2'-methoxyethoxy)-1-naphthyltetrahydrothiophenium-
trifluoromethanesulfonate,
4-(2'-methoxyethoxy)-1-naphthyltetrahydrothiophenium-
nonafluoro-n-butanesulfonate,
4-(2'-methoxyethoxy)-1-naphthyltetrahydrothiophenium-
perfluoro-n-octanesulfonate,
4-methoxycarbonyloxy-1-naphthyltetrahydrothiophenium-
trifluoromethanesulfonate,
4-methoxycarbonyloxy-1-naphthyltetrahydrothiophenium-
nonafluoro-n-butanesulfonate,
4-methoxycarbonyloxy-1-naphthyltetrahydrothiophenium-
perfluoro-n-octanesulfonate,
4-ethoxycarbonyloxy-1-naphthyltetrahydrothiophenium-
trifluoromethanesulfonate,
4-ethoxycarbonyloxy-1-naphthyltetrahydrothiophenium-
nonafluoro-n-butanesulfonate,
4-ethoxycarbonyloxy-1-naphthyltetrahydrothiophenium-
perfluoro-n-octanesulfonate,
4-n-propoxycarbonyloxy-1-naphthyltetrahydrothiophenium-
trifluoromethanesulfonate,
4-n-propoxycarbonyloxy-1-naphthyltetrahydrothiophenium-

nonafluoro-n-butanesulfonate,
4-n-propoxycarbonyloxy-1-naphthyltetrahydrothiophenium-
perfluoro-n-octanesulfonate,
4-i-propoxycarbonyloxy-1-naphthyltetrahydrothiophenium-
trifluoromethanesulfonate,
4-i-propoxycarbonyloxy-1-naphthyltetrahydrothiophenium-
nonafluoro-n-butanesulfonate,
4-i-propoxycarbonyloxy-1-naphthyltetrahydrothiophenium-
perfluoro-n-octanesulfonate,

[0122]

4-n-butoxycarbonyloxy-1-naphthyltetrahydrothiophenium-
trifluoromethanesulfonate,
4-n-butoxycarbonyloxy-1-naphthyltetrahydrothiophenium-
nonafluoro-n-butanesulfonate,
4-n-butoxycarbonyloxy-1-naphthyltetrahydrothiophenium-
perfluoro-n-octanesulfonate,
4-t-butoxycarbonyloxy-1-naphthyltetrahydrothiophenium-
trifluoromethanesulfonate,
4-t-butoxycarbonyloxy-1-naphthyltetrahydrothiophenium-
nonafluoro-n-butanesulfonate,
4-t-butoxycarbonyloxy-1-naphthyltetrahydrothiophenium-
perfluoro-n-octanesulfonate,
4-(2'-tetrahydrofuranyloxy)-1-naphthyltetrahydrothiophenium
trifluoromethanesulfonate,
4-(2'-tetrahydrofuranyloxy)-1-naphthyltetrahydrothiophenium
nonafluoro-n-butanesulfonate,
4-(2'-tetrahydrofuranyloxy)-1-naphthyltetrahydrothiophenium

perfluoro-n-octanesulfonate,
4-(2'-tetrahydropyranyloxy)-1-naphthyltetrahydrothiophenium
trifluoromethanesulfonate,
4-(2'-tetrahydropyranyloxy)-1-naphthyltetrahydrothiophenium
nonafluoro-n-butanesulfonate,
4-(2'-tetrahydropyranyloxy)-1-naphthyltetrahydrothiophenium
perfluoro-n-octanesulfonate,
4-benzyloxy-1-naphthyltetrahydrothiopheniumtrifluoromethane
sulfonate,
4-benzyloxy-1-naphthyltetrahydrothiopheniumnonafluoro-
n-butanesulfonate,
4-benzyloxy-1-naphthyltetrahydrothiopheniumperfluoro-
n-octanesulfonate,
1-(1'-naphthylacetomethyl)tetrahydrothiopheniumtrifluoro-
methanesulfonate,
1-(1'-naphthylacetomethyl)tetrahydrothiopheniumnonafluoro-
n-butanesulfonate,
1-(1'-naphthylacetomethyl)tetrahydrothiopheniumperfluoro-
n-octanesulfonate,
1-(3,5-dimethyl-4-hydroxyphenyl)tetrahydrothiophenium-
trifluoromethanesulfonate,
1-(3,5-dimethyl-4-hydroxyphenyl)tetrahydrothiophenium-
nonafluoro-n-butanesulfonate, and
1-(3,5-dimethyl-4-hydroxyphenyl)tetrahydrothiophenium-
perfluoro-n-octanesulfonate,

[0123]

Halogen-containing compounds:

As examples of halogen-containing compounds, haloalkyl group-containing hydrocarbon compounds, haloalkyl group-containing heterocyclic compounds, and the like can be given.

As specific examples of preferable halogen-containing compounds, (trichloromethyl)-s-triazine derivatives such as phenylbis(trichloromethyl)-s-triazine, 4-methoxyphenylbis(trichloromethyl)-s-triazine, and 1-naphthylbis(trichloromethyl)-s-triazine, 1,1-bis(4'-chlorophenyl)-2,2,2-trichloroethane, and the like can be given.

Diazoketone compounds:

As examples of diazoketone compounds, 1,3-diketo-2-diazo compounds, diazobenzoquinone compounds, diazonaphthoquinone compounds, and the like can be given.

As specific examples of preferable diazoketone compounds, 1,2-naphthoquinonediazido-4-sulfonyl chloride, 1,2-naphthoquinonediazido-5-sulfonyl chloride, 1,2-naphthoquinonediazido-4-sulfonate or 1,2-naphthoquinonediazido-5-sulfonate of 2,3,4,4'-tetrahydroxybenzophenone, 1,2-naphthoquinonediazido-4-sulfonate or 1,2-naphthoquinonediazido-5-sulfonate of 1,1,1-tris(4'-hydroxyphenyl)ethane, and the like can be given.

[0124]

Sulfone compounds:

As examples of sulfone compounds, β -ketosulfone,

β -sulfonylsulfone, α -diazo compounds of these compounds, and the like can be given.

As specific examples of preferable sulfone compounds, 4-trisphenacylsulfone, mesitylphenacylsulfone, bis(phenylsulfonyl)methane, and the like can be given.

Sulfonate compounds:

As examples of sulfonate compounds, alkyl sulfonate, alkylimide sulfonate, haloalkyl sulfonate, aryl sulfonate, imino sulfonate, and the like can be given.

As specific examples of preferable sulfonate compounds, benzointosylate, tris(trifluoromethanesulfonate) of pyrogallol, nitrobenzyl-9,10-diethoxyanthracene-2-sulfonate, trifluoromethanesulfonylbicyclo[2.2.1]hept-5-ene-2,3-dicarbodiimide, nonafluoro-n-butanesulfonylbicyclo[2.2.1]hept-5-ene-2,3-dicarbodiimide, perfluoro-n-octanesulfonylbicyclo[2.2.1]hept-5-ene-2,3-dicarbodiimide, N-hydroxysuccinimide-trifluoromethanesulfonate, N-hydroxysuccinimide-nonafluoro-n-butanesulfonate, N-hydroxysuccinimide-perfluoro-n-octanesulfonate, 1,8-naphthalenedicarboxylic acid imide trifluoromethanesulfonate, and the like can be given.

[0125]

Of these acid generators (B), the following compounds are particularly preferable:

diphenyliodoniumtrifluoromethanesulfonate,

diphenyliodoniumnonafluoro-n-butanesulfonate,
diphenyliodoniumperfluoro-n-octanesulfonate,
bis(4-t-butylphenyl)iodoniumtrifluoromethanesulfonate,
bis(4-t-butylphenyl)iodoniumnonafluoro-n-butanesulfonate,
bis(4-t-butylphenyl)iodoniumperfluoro-n-octanesulfonate,
triphenylsulfoniumtrifluoromethanesulfonate,
triphenylsulfoniumnonafluoro-n-butanesulfonate,
triphenylsulfoniumperfluoro-n-octanesulfonate,
cyclohexyl·2-oxocyclohexyl·methylsulfoniumtrifluoromethane-
sulfonate,
dicyclohexyl·2-oxocyclohexylsulfoniumtrifluoromethane-
sulfonate,
2-oxocyclohexyldimethylsulfoniumtrifluoromethanesulfonate,
4-hydroxy-1-naphthyl dimethylsulfoniumtrifluoromethane-
sulfonate,

[0126]

4-hydroxy-1-naphthyltetrahydrothiopheniumtrifluoromethane-
sulfonate,
4-hydroxy-1-naphthyltetrahydrothiopheniumnonafluoro-
n-butanesulfonate,
4-hydroxy-1-naphthyltetrahydrothiopheniumperfluoro-
n-octanesulfonate,
1-(1'-naphthylacetomethyl)tetrahydrothiopheniumtrifluoro-
methanesulfonate,
1-(1'-naphthylacetomethyl)tetrahydrothiopheniumnonafluoro-
n-butanesulfonate,
1-(1'-naphthylacetomethyl)tetrahydrothiopheniumperfluoro-

n-octanesulfonate,

1-(3,5-dimethyl-4-hydroxyphenyl)tetrahydrothiophenium-
trifluoromethanesulfonate,

1-(3,5-dimethyl-4-hydroxyphenyl)tetrahydrothiophenium-
nonafluoro-n-butanesulfonate,

1-(3,5-dimethyl-4-hydroxyphenyl)tetrahydrothiophenium-
perfluoro-n-octanesulfonate,

[0127]

trifluoromethanesulfonylbicyclo[2.2.1]hept-5-ene-2,3-
dicarbodiimide,

nonafluoro-n-butanesulfonylbicyclo[2.2.1]hept-5-ene-2,3-
dicarbodiimide,

perfluoro-n-octanesulfonylbicyclo[2.2.1]hept-5-ene-2,3-
dicarbodiimide,

N-hydroxysuccimidetrifluoromethanesulfonate,

N-hydroxysuccimidenonafluoro-n-butanesulfonate,

N-hydroxysuccimideperfluoro-n-octanesulfonate, and

1,8-naphthalene dicarboxylic acid

imidetrifluoromethanesulfonate,

[0128]

In the present invention, the acid generator (B) may be used either individually or in combination of two or more.

The amount of the acid generator (B) to be used in the present invention is usually 0.1-10 parts by weight, and preferably 0.5-7 parts by weight for 100 parts by weight of the resin (A) from the viewpoint of ensuring sensitivity and developability as a resist. If the amount of the acid generator

(B) is less than 0.1 part by weight, sensitivity and developability tend to decrease. If the amount exceeds 10 parts by weight, a rectangular resist pattern may not be obtained due to decreased radiation transmittance.

[0129]

Additives

It is preferable to add an acid diffusion controller to the radiation-sensitive resin composition of the present invention. The acid diffusion controller controls diffusion of an acid generated from the acid generator (B) upon exposure in the resist film to hinder unfavorable chemical reactions in the unexposed area.

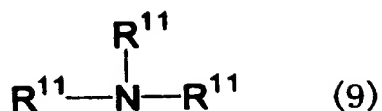
The addition of such an acid diffusion controller improves storage stability of the resulting radiation-sensitive resin composition and resolution as a resist. Moreover, the addition of the acid diffusion controller prevents the line width of the resist pattern from changing due to changes in the post-exposure delay (PED) between exposure and development, whereby a composition with remarkably superior process stability can be obtained.

As the acid diffusion controller, organic compounds containing nitrogen of which the basicity does not change during exposure or heating for forming a resist pattern are preferable.

As examples of such nitrogen-containing organic compounds, compounds shown by the following formula (9) (hereinafter called "nitrogen-containing compounds (a)"),

[0130]

[Formula 37]



wherein R^{11} individually represents a hydrogen atom, a substituted or unsubstituted, linear, branched, or cyclic alkyl group, substituted or unsubstituted aryl group, or substituted or unsubstituted aralkyl group,

[0131]

compounds having two nitrogen atoms in the molecule (hereinafter called "nitrogen-containing compounds (b)"), polyamino compounds or polymers having three or more nitrogen atoms (hereinafter collectively called "nitrogen-containing compounds (c)"), amide group-containing compounds, urea compounds, nitrogen-containing heterocyclic compounds, and the like can be given.

[0132]

Examples of the nitrogen-containing compounds (a) include mono(cyclo)alkylamines such as n-hexylamine, n-heptylamine, n-octylamine, n-nonylamine, n-decylamine, and cyclohexylamine; di(cyclo)alkylamines such as di-n-butylamine, di-n-pentylamine, di-n-hexylamine, di-n-heptylamine, di-n-octylamine, di-n-nonylamine, di-n-decylamine, cyclohexylmethanamine, and dicyclohexylamine; tri(cyclo)alkylamines such as triethylamine, tri-n-propylamine, tri-n-butylamine, tri-n-pentylamine,

tri-n-hexylamine, tri-n-heptylamine, tri-n-octylamine, tri-n-nonylamine, tri-n-decylamine, cyclohexyldimethylamine, dicyclohexylmethylamine, and tricyclohexylamine; aromatic amines such as aniline, N-methylaniline, N,N-dimethylaniline, 2-methylaniline, 3-methylaniline, 4-methylaniline, 4-nitroaniline, diphenylamine, triphenylamine, and naphthylamine; and the like.

[0133]

Examples of the nitrogen-containing compound (b) include ethylenediamine, N,N,N',N'-tetramethylethylenediamine, tetramethylenediamine, hexamethylenediamine, 4,4'-diaminodiphenylmethane, 4,4'-diaminodiphenyl ether, 4,4'-diaminobenzophenone, 4,4'-diaminodiphenylamine, 2,2-bis(4'-aminophenyl)propane, 2-(3'-aminophenyl)-2-(4'-aminophenyl)propane, 2-(4'-aminophenyl)-2-(3'-hydroxyphenyl)propane, 2-(4'-aminophenyl)-2-(4'-hydroxyphenyl)propane, 1,4-bis[1'-(4''-aminophenyl)-1'-methylethyl]benzene, 1,3-bis[1'-(4''-aminophenyl)-1'-methylethyl]benzene, bis(2-dimethylaminoethyl)ether, bis(2-diethylaminoethyl)ether, and the like.

Examples of the nitrogen-containing compounds (c) include polyethyleneimine, polyallylamine, a polymer of 2-dimethylaminoethylacrylamide, and the like.

[0134]

Examples of the amide group-containing compound include, in addition to N-t-butoxycarbonyl group-containing amino

compounds, such as N-t-butoxycarbonyl di-n-octylamine, N-t-butoxycarbonyl di-n-nonylamine, N-t-butoxycarbonyl di-n-decylamine, N-t-butoxycarbonyl dicyclohexylamine, N-t-butoxycarbonyl-1-adamantylamine, N-t-butoxycarbonyl-N-methyl-1-adamantylamine, N,N-di-t-butoxycarbonyl-1-adamantylamine, N,N-di-t-butoxycarbonyl-N-methyl-1-adamantylamine, N-t-butoxycarbonyl-4,4'-diaminodiphenylmethane, N,N'-di-t-butoxycarbonylhexamethylenediamine, N,N,N',N'-tetra-t-butoxycarbonylhexamethylenediamine, N,N'-di-t-butoxycarbonyl-1,7-diaminoheptane, N,N'-di-t-butoxycarbonyl-1,8-diaminooctane, N,N'-di-t-butoxycarbonyl-1,9-diaminononane, N,N'-di-t-butoxycarbonyl-1,10-diaminodecane, N,N'-di-t-butoxycarbonyl-1,12-diaminododecane, N,N'-di-t-butoxycarbonyl-4,4'-diaminodiphenylmethane, N-t-butoxycarbonylbenzimidazole, N-t-butoxycarbonyl-2-methylbenzimidazole, and N-t-butoxycarbonyl-2-phenylbenzimidazole, formamide, N-methylformamide, N,N-dimethylformamide, acetamide, N-methylacetamide, N,N-dimethylacetamide, propionamide, benzamide, pyrrolidone, N-methylpyrrolidone; and the like.

[0135]

Examples of the urea compounds include urea, methylurea, 1,1-dimethylurea, 1,3-dimethylurea, 1,1,3,3-tetramethylurea, 1,3-diphenylurea, tri-n-butylthiourea, and the like.

Examples of the nitrogen-containing heterocyclic compounds include: imidazoles such as imidazole, benzimidazole, 4-methylimidazole, and 4-methyl-2-phenylimidazole; pyridines such as pyridine, 2-methylpyridine, 4-methylpyridine, 2-ethylpyridine, 4-ethylpyridine, 2-phenylpyridine, 4-phenylpyridine, 2-methyl-4-phenylpyridine, nicotine, nicotinic acid, nicotinamide, quinoline, 4-hydroxyquinoline, 8-oxyquinoline, and acridine; piperazines such as piperazine, 1-(2'-hydroxyethyl)piperazine; pyrazine, pyrazole, pyridazine, quinoxaline, purine, pyrrolidine, piperidine, 3-piperidino-1,2-propanediol, morpholine, 4-methylmorpholine, 1,4-dimethylpiperazine, and 1,4-diazabicyclo[2.2.2]octane; and the like.

[0136]

Of these nitrogen-containing organic compounds, the nitrogen-containing compounds (a), nitrogen-containing compounds (b), and nitrogen-containing heterocyclic compounds are preferable.

The acid diffusion controller may be used either individually or in combination of two or more.

The amount of the acid diffusion controller to be added is usually 15 parts by weight or less, preferably 10 parts by weight or less, and still more preferably 5 parts by weight or less for 100 parts by weight of the resin (A). If the proportion of the acid diffusion controller exceeds 15 parts by weight, sensitivity as a resist and developability of the exposed area tend to decrease. If the amount is less than 0.001 part by

weight, the pattern shape or dimensional accuracy as a resist may decrease depending on the processing conditions.

[0137]

Alicyclic additives having an acid-dissociating group which further improve dry etching resistance, pattern shape, adhesion to substrate, or the like may be added to the radiation-sensitive resin composition of the present invention.

Examples of such alicyclic additives include:

adamantane derivatives such as t-butyl
1-adamantanecarboxylate, t-butoxycarbonylmethyl
1-adamantanecarboxylate, di-t-butyl
1,3-adamantanedicarboxylate, t-butyl 1-adamantaneacetate,
t-butoxycarbonylmethyl 1-adamantaneacetate, and di-t-butyl
1,3-adamantanediacetate;
deoxycholates such as t-butyl deoxycholate,
t-butoxycarbonylmethyl deoxycholate, 2-ethoxyethyl
deoxycholate, 2-cyclohexyloxyethyl deoxycholate,
3-oxocyclohexyl deoxycholate, tetrahydropyranyl deoxycholate,
and mevalonolactone deoxycholate;
lithocholates such as t-butyl lithocholate,
t-butoxycarbonylmethyl lithocholate, 2-ethoxyethyl
lithocholate, 2-cyclohexyloxyethyl lithocholate,
3-oxocyclohexyl lithocholate, tetrahydropyranyl lithocholate,
and mevalonolactone lithocholate; and the like.

These alicyclic additives may be used either individually or in combination of two or more.

The amount of the alicyclic additives to be added is usually 50 parts by weight or less, and preferably 30 parts by weight or less for 100 parts by weight of the resin (A). If the amount of alicyclic additives exceeds 50 parts by weight, heat resistance as a resist tends to decrease.

[0138]

Surfactants which improve applicability, developability, or the like may be added to the radiation-sensitive resin composition of the present invention.

As examples of surfactants, nonionic surfactants such as polyoxyethylene lauryl ether, polyoxyethylene stearyl ether, polyoxyethylene oleyl ether, polyoxyethylene n-octyl phenyl ether, polyoxyethylene n-nonyl phenyl ether, polyethylene glycol dilaurate, polyethylene glycol distearate; commercially available products such as KP341 (manufactured by Shin-Etsu Chemical Co., Ltd.), Polyflow No. 75, No. 95 (manufactured by Kyoeisha Chemical Co., Ltd.), FTOP EF301, EF303, EF352 (manufactured by TOHKEM PRODUCTS CORPORATION), MEGAFAC F171, F173 (manufactured by Dainippon Ink and Chemicals, Inc.), Fluorard FC430, FC431 (manufactured by Sumitomo 3M Ltd.), Asahi Guard AG710, Surflon S-382, SC-101, SC-102, SC-103, SC-104, SC-105, SC-106 (manufactured by Asahi Glass Co., Ltd.); and the like can be given.

These surfactants may be used either individually or in combination of two or more.

The amount of surfactants to be added is usually 2 parts by weight or less for 100 parts by weight of the total of the

resin (A) and the acid generator (B).

As other additives, halation inhibitors, adhesion promoters, storage stabilizers, anti-foaming agents, and the like can be given.

[0139]

Preparation of composition solution

The radiation-sensitive resin composition of the present invention is prepared as a composition solution by dissolving the composition in a solvent so that the total solid content is 5-50 wt%, and preferably 10-25 wt%, and filtering the composition using a filter with a pore diameter of about 0.2 μm , for example.

Examples of solvents used for the preparation of the composition solution include: linear or branched ketones such as 2-butanone, 2-pentanone, 3-methyl-2-butanone, 2-hexanone, 4-methyl-2-pentanone, 3-methyl-2-pentanone, 3,3-dimethyl-2-butanone, 2-heptanone, and 2-octanone; cyclic ketones such as cyclopentanone, 3-methylcyclopentanone, cyclohexanone, 2-methylcyclohexanone, 2,6-dimethylcyclohexanone, and isophorone; propylene glycol monoalkyl ether acetates such as propylene glycol monomethyl ether acetate, propylene glycol monoethyl ether acetate, propylene glycol mono-n-propyl ether acetate, propylene glycol mono-i-propyl ether acetate, propylene glycol mono-n-butyl ether acetate, propylene glycol mono-i-butyl ether acetate, propylene glycol mono-sec-butyl ether acetate, and propylene glycol mono-t-butyl ether acetate;

alkyl 2-hydroxypropionates such as methyl 2-hydroxypropionate, ethyl 2-hydroxypropionate, n-propyl 2-hydroxypropionate, i-propyl 2-hydroxypropionate, n-butyl 2-hydroxypropionate, i-butyl 2-hydroxypropionate, sec-butyl 2-hydroxypropionate, and t-butyl 2-hydroxypropionate;

alkyl 3-alkoxypropionates such as methyl 3-methoxypropionate, ethyl 3-methoxypropionate, methyl 3-ethoxypropionate, and ethyl 3-ethoxypropionate;

[0140]

as well as other solvents such as n-propyl alcohol, i-propyl alcohol, n-butyl alcohol, t-butyl alcohol, cyclohexanol, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol mono-n-propyl ether, ethylene glycol mono-n-butyl ether, diethylene glycol dimethyl ether, diethylene glycol diethyl ether, diethylene glycol di-n-propyl ether, diethylene glycol di-n-butyl ether, ethylene glycol monomethyl ether acetate, ethylene glycol monoethyl ether acetate, ethylene glycol mono-n-propyl ether acetate, propylene glycol monomethyl ether, propylene glycol monoethyl ether, propylene glycol mono-n-propyl ether, toluene, xylene, 2-hydroxy-2-methylethyl propionate, ethoxyethyl acetate, ethyl hydroxyacetate, methyl 2-hydroxy-3-methylbutyrate, 3-methoxybutylacetate, 3-methyl-3-methoxybutylacetate, 3-methyl-3-methoxybutylpropionate, 3-methyl-3-methoxybutylbutyrate, ethyl acetate, n-propyl acetate, n-butylacetate, methyl acetoacetate, ethyl acetoacetate, methyl pyruvate, ethyl pyruvate, N-methyl

pyrrolidone, N,N-dimethylformamide, N,N-dimethylacetamide, benzyl ethyl ether, di-n-hexyl ether, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, caproic acid, caprylic acid, 1-octanol, 1-nonanol, benzyl alcohol, benzyl acetate, ethyl benzoate, diethyl oxalate, diethyl maleate, γ -butyrolactone, ethylene carbonate, and propylene carbonate.

[0141]

These solvents may be used either individually or in combination of two or more. Among these solvents, linear or branched ketones, cyclic ketones, propylene glycol monoalkyl ether acetates, alkyl 2-hydroxypropionates, and alkyl 3-alkoxypropionates are preferable.

[0142]

Formation of resist pattern

The radiation-sensitive resin composition of the present invention is particularly useful as a chemically-amplified resist.

In the chemically-amplified resist, an acid-dissociating group in the resin (A) dissociates by the action of an acid generated from the acid generator (B) upon exposure, thereby producing an acidic functional group, preferably a carboxyl group. As a result, solubility of the exposed area of the resist in an alkaline developer increases, whereby the exposed area is dissolved in an alkaline developer and removed to obtain a positive-tone resist pattern.

A resist pattern is formed from the radiation-sensitive

resin composition of the present invention by applying the composition solution to, for example, substrates such as a silicon wafer or a wafer coated with aluminum using an appropriate application method such as spin coating, cast coating, and roll coating to form a resist film. The resist film is then optionally pre-baked (hereinafter called "PB") and exposed to form a predetermined resist pattern. As radiation used for exposure, visible rays, ultraviolet rays, deep ultraviolet rays, X-rays, charged particle beams, or the like is appropriately selected depending on types of the acid generator. It is particularly preferable to use an ArF excimer laser (wavelength: 193 nm) or KrF excimer laser (wavelength: 248 nm).

In the present invention, it is preferable to perform post-exposure bake (hereinafter called "PEB") after exposure. PEB ensures smooth dissociation of the acid-dissociating organic group in the resin (A). The heating temperature for PEB is usually 30-200°C, and preferably 50-170°C, although the heating conditions vary depending on the composition of the radiation-sensitive resin composition.

[0143]

In order to bring out latent capability of the radiation-sensitive resin composition of the present invention, an organic or inorganic anti-reflection film may be formed on a substrate as disclosed in Japanese Patent Publication No. 12452/1994, for example. Moreover, a protection film may be formed on the resist film as disclosed in Japanese Patent

Publication No. 188598/1993 or the like in order to prevent the effects of basic impurities or the like in an environmental atmosphere. These techniques may be employed in combination.

The exposed resist film is then developed to form a predetermined resist pattern.

As examples of a developer used for development, it is preferable to use an alkaline aqueous solution prepared by dissolving at least one of alkaline compounds such as sodium hydroxide, potassium hydroxide, sodium carbonate, sodium silicate, sodium metasilicate, aqueous ammonia, ethylamine, n-propylamine, diethylamine, di-n-propylamine, triethylamine, methyldiethylamine, ethyldimethylamine, triethanolamine, tetramethylammonium hydroxide, pyrrole, piperidine, choline, 1,8-diazabicyclo-[5.4.0]-7-undecene, and 1,5-diazabicyclo-[4.3.0]-5-nonene.

The concentration of the alkaline aqueous solution is usually 10 wt% or less. If the concentration of the alkaline aqueous solution exceeds 10 wt%, an unexposed area may be dissolved in the developer.

[0144]

Organic solvents or the like may be added to the developer containing an alkaline aqueous solution.

As examples of organic solvents, linear, branched, or cyclic ketones such as acetone, methyl ethyl ketone, methyl i-butyl ketone, cyclopentanone, cyclohexanone, 3-methylcyclopentanone, and 2,6-dimethylcyclohexanone; alcohols such as methylalcohol, ethylalcohol, n-propylalcohol,

i-propylalcohol, n-butylalcohol, t-butylalcohol, cyclopentanol, cyclohexanol, 1,4-hexanediol, and 1,4-hexanedimethylol; ethers such as tetrahydrofuran and dioxane; esters such as ethyl acetate, n-butyl acetate, and i-amyl acetate; aromatic hydrocarbons such as toluene and xylene; phenol, acetonylacetone, dimethylformamide; and the like can be given.

These organic solvents may be used either individually or in combination of two or more.

The amount of the organic solvents is preferably 100 vol% or less of the alkaline aqueous solution. If the amount of the organic solvents exceeds 100 vol%, an exposed area may remain undeveloped due to decreased developability.

In addition, surfactants or the like may be added to the developer containing the alkaline aqueous solution in an appropriate amount.

The resist film is generally washed with water after development using a developer containing an alkaline aqueous solution.

[0145]

[Detailed Description of the Invention and Preferred Embodiments]

The embodiments of the present invention will be described in more detail by examples. However, these examples should not be construed as limiting the present invention. In the examples, part(s) refers to part(s) by weight unless otherwise indicated.

Measurement and evaluation of each composition in the examples and comparative examples were carried out as follows.

Mw:

Mw was measured by gel permeation chromatography (GPC) using GPC columns (manufactured by Tosoh Corp., G2000HXL x 2, G3000HXL x 1, G4000HXL x 1) under the following conditions. Flow rate: 1.0 ml/minute, eluate: tetrahydrofuran, column temperature: 40°C, standard reference material: monodispersed polystyrene

Radiation transmittance:

A solution composition was applied to a quartz plate by spin coating and the coating was post-baked on a hot plate at 90°C for 60 seconds to obtain a resist coating with a thickness of 1 μm . Radiation transmittance of the resist coating was calculated from absorbance at a wavelength of 193 nm and was adopted as a standard for transparency in the deep UV ray region.

Sensitivity:

A solution composition was applied to a silicon wafer with a 520Å thickness Deep UV30 (ARC) film (manufactured by Brewer Science Inc.) formed on the surface by spin coating and post-baked on a hot plate under the conditions shown in Table 2 to obtain a resist coating with a thickness of 0.4 μm . The coating was exposed to radiation through a mask pattern using an ArF excimer laser exposure apparatus (manufactured by Nikon Corp., lens numerical aperture: 0.55, wavelength: 193 nm). After PEB under the conditions shown in Table 2, the resist coatings were developed in a 2.38 wt% tetramethylammonium

hydroxide aqueous solution (Examples 1-6) or 2.38 x 1/50 wt% tetramethylammonium hydroxide aqueous solution (Comparative Example 1) at 25°C for 1 minute, washed with water, and dried to form a positive-tone resist pattern. An optimum dose at which a line-and-space (1L1S) pattern with a line width of 0.18 μm was formed was taken as sensitivity.

[0146]

Resolution:

Minimum dimensions of the resist pattern resolved at the optimum dose was taken as the resolution of the resist coating.

Defect:

Defect was evaluated by observing the presence or absence of the defective development using an optical microscope and a KLA defect inspection device (manufactured by KLA-TENCOR JAPAN LTD.) by the following procedure.

Evaluation procedure using KLA defect inspection device:

The total number of defective clusters and unclusters in one piece of wafer extracted from the difference produced by superposing reference images and pixels was counted by array mode observation using the KLA defect inspection device of which the sensitivity was set to detect defects with a size 0.15 μm or greater.

Pattern configuration:

The length of the bottom (L_1) and top (L_2) of a square cross-section of a line-and-space (1L1S) pattern with a line width of 0.20 μm was measured by a scanning electron microscope.

The pattern configuration was judged as "Good" when 0.85

$\leq L_2/L_1 \leq 1$ was satisfied and the pattern was not tapered.

[0147]

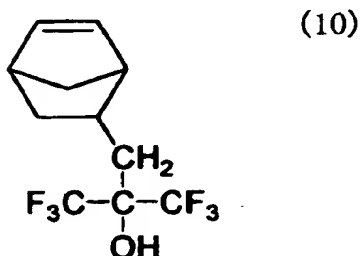
Synthesis of monomers

Synthesis Example 1

A 500 ml autoclave was charged with 22 g of cyclopentadiene, 109 g of 1,1-bis(trifluoromethyl)-3-butenol, and 450 mg of hydroquinone in an argon atmosphere, and the mixture was heated at 170°C for 17 hours. The reaction solution was distilled to obtain 70 g of 5-[2,2-bis(trifluoromethyl)-2-hydroxyethyl]bicyclo[2.2.1]-hept-2-ene of the following formula (10).

[0148]

[Formula 38]



[0149]

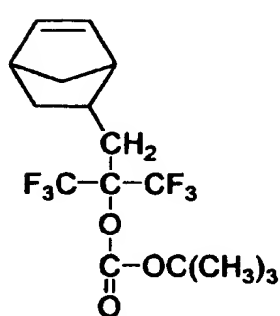
Synthesis Example 2

A 500 ml reaction vessel was charged with 10 g of 5-[2,2-bis(trifluoromethyl)-2-hydroxyethyl]bicyclo[2.2.1]-hept-2-ene obtained in Synthesis Example 1, 10 g of potassium carbonate, 40 g of tetrahydrofuran, and 20 g of water. After the addition of 8 g of t-butyl bromoacetate, the mixture was

reacted at 70°C for six hours. The reaction mixture was mixed with 200 ml of ethyl acetate and the mixture was washed with water. The solvent was removed under reduced pressure to obtain a crude product. The crude product was distilled under reduced pressure to obtain 7 g of 5-[2,2-bis(trifluoromethyl)-2-t-butoxycarbonyloxyethyl]bicyclo[2.2.1]hept-2-ene of the following formula (11).

[0150]

[Formula 39]



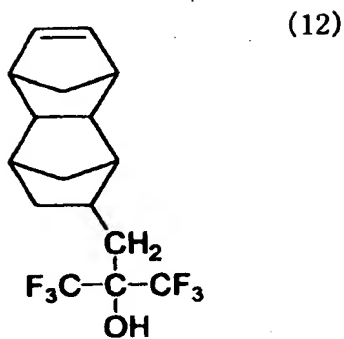
[0151]

Synthesis Example 3

A 500 ml autoclave was charged with 230 g of 1,1-bis(trifluoromethyl)-3-butenol, 73 g of dicyclopentadiene, and 0.15 g of 2,6-di-t-butylparacresol, and the mixture was heated at 190°C for 12 hours. The reaction solution was cooled to room temperature and purified by distillation to obtain 40 g of 8-(2,2,2-trifluoro-1-trifluoromethyl-1-hydroxyethyl)tetracyclo[4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene of the following formula (12).

[0152]

[Formula 40]



[0153]

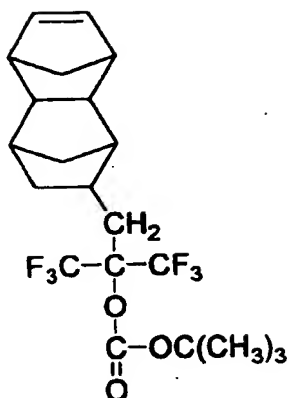
Synthesis Example 4

6 g of 8-[2,2-bis(trifluoromethyl)-2-t-butoxycarbonyloxyethyl]tetracyclo[4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene of the following formula (13) was prepared in the same manner as in the Synthesis Example 2 except for using 10 g of 8-(2,2,2-trifluoro-1-trifluoromethyl-1-hydroxyethyl)tetracyclo[4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene obtained in the Synthesis Example 3 instead of 5-[2,2-bis(trifluoromethyl)-2-hydroxyethyl]bicyclo[2.2.1]hept-2-ene.

[0154]

[Formula 41]

(13)



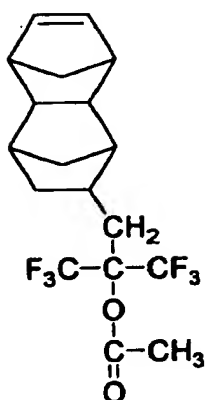
[0155]

Synthesis Example 5

10 g of 8-(2,2,2-trifluoro-1-trifluoromethyl-1-hydroxyethyl)tetracyclo[4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene obtained in the Synthesis Example 3 was refluxed for 24 hours in acetic anhydride and the crude product obtained was purified by distillation to obtain 6 g of 8-[2,2-bis(trifluoromethyl)-2-methylcarbonyloxyethyl]-tetracyclo[4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene of the following formula (14).

[0156]

[Formula 42]



[0157]

Synthesis of resin (A)

Synthesis Example 6

A 100 ml pressure polymerization bottle was charged with 15 ml of 1,2-dichloroethane, 4.5 g of 5-[2,2-bis(trifluoromethyl)-2-hydroxyethyl]bicyclo[2.2.1]hept-2-ene, and 2.4 g of 5-[2,2-bis(trifluoromethyl)-2-t-butoxycarbonyloxyethyl]bicyclo[2.2.1]hept-2-ene. 2 ml of a solution of palladium complex catalyst prepared by the method described below was added to initiate the polymerization reaction. The reaction was continued for 6 hours at 30°C. The reaction solution was charged into a large amount of methanol to coagulate the product, which was filtered to obtain 4.7 g of a resin.

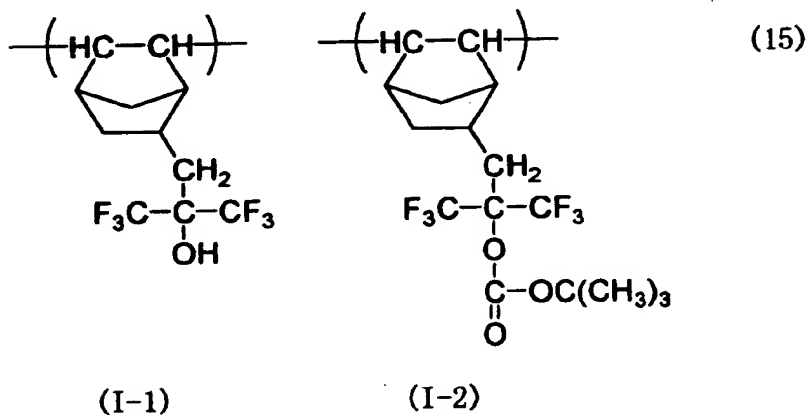
The resin was confirmed to be a copolymer with a copolymerization molar ratio of the recurring unit (I-1) and recurring unit (I-2), shown in the following formula (15), of 65:35, and having Mw of 6,000. This resin is referred to as a "resin (A-1)".

<Preparation of catalyst>

A solution of 40 mg of silver hexafluoroantimonate dissolved in 1 ml of 1,2-dichloroethane was added to a solution of 27 mg of π -allyl palladium chloride dimer in 1 ml of 1,2-dichloroethane. The mixture was stirred for one hour at room temperature and silver chloride formed was separated by filtration to obtain a solution of palladium complex catalyst in 1,2-dichloroethane.

[0158]

[Formula 43]



[0159]

Synthesis Example 7

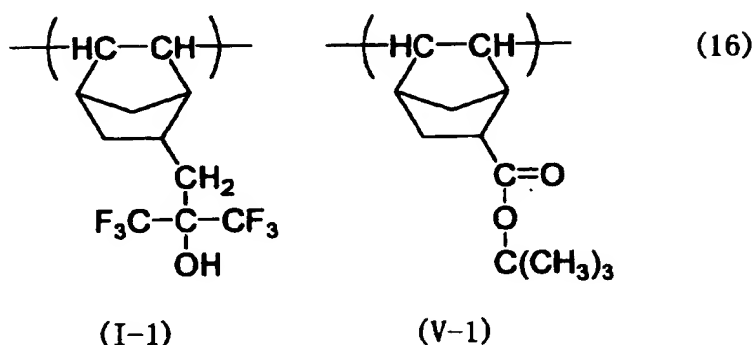
The same polymerization reaction as in the Synthesis Example 6 was carried out, except for using 5.4 g of 5-[2,2-bis(trifluoromethyl)-2-hydroxyethyl]bicyclo[2.2.1]-hept-2-ene and 2.1 g of 5-t-butoxycarbonylbicyclo[2.2.1]-hept-2-ene as monomers, to obtain 5.1 g of a resin.

The resin was confirmed to be a copolymer with a

copolymerization molar ratio of the recurring unit (I-1) and recurring unit (V-1), shown in the following formula (16), of 65:35, and having Mw of 6,200. This resin is referred to as a "resin (A-2)".

[0160]

[Formula 44]



[0161]

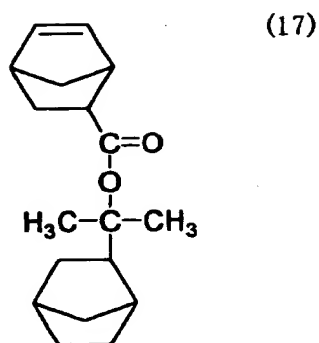
Synthesis Example 8

The same polymerization reaction as in the Synthesis Example 6 was carried out, except for using 4.9 g of 5-[2,2-bis(trifluoromethyl)-2-hydroxyethyl]bicyclo[2.2.1]-hept-2-ene and 2.6 g of the compound shown by the following formula (17) as monomers, to obtain 4.9 g of a resin.

The resin was confirmed to be a copolymer with a copolymerization molar ratio of the recurring unit (I-1) and recurring unit (V-2), shown in the following formula (18), of 65:35, and having Mw of 5,800. This resin is referred to as a "resin (A-3)".

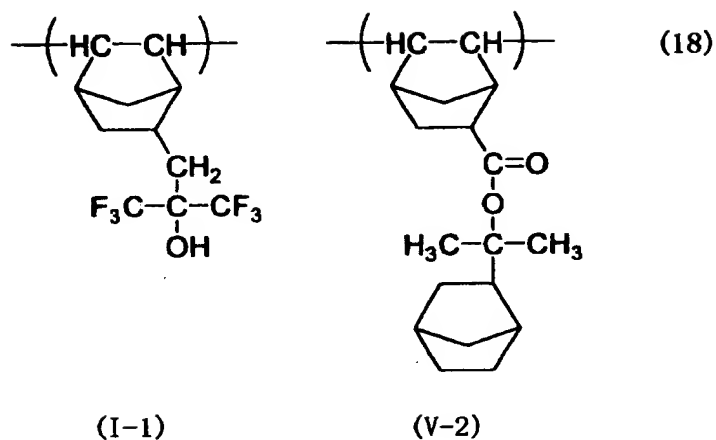
[0162]

[Formula 45]



[0163]

[Formula 46]



[0164]

Synthesis Example 9

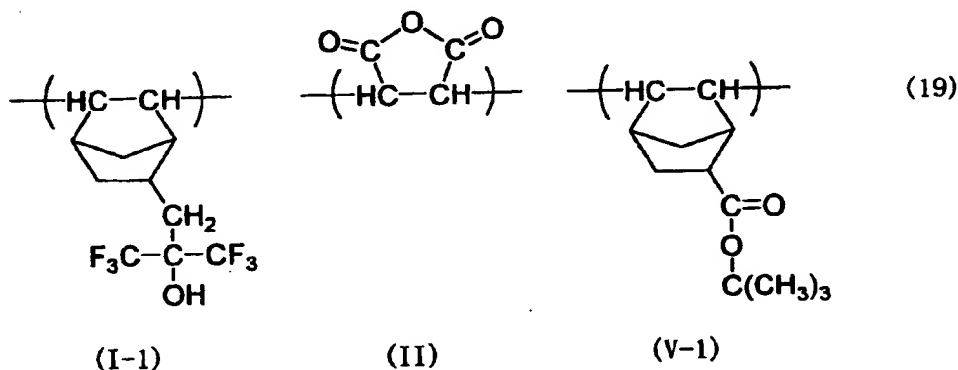
A 100 ml eggplant flask was charged with 12.1 g of 5-[2,2-bis(trifluoromethyl)-2-hydroxyethyl]bicyclo[2.2.1]hept-2-ene, 5.7 g of 5-t-butoxycarbonylbicyclo[2.2.1]hept-2-ene, 7.2 g of maleic anhydride, 1.5 g of azobisisobutyronitrile, and 25 g of tetrahydrofuran in a nitrogen atmosphere. The mixture was reacted at 60°C for eight hours. After polymerization, the reaction solution was cooled

to room temperature and poured into a large quantity of a isopropylalcohol/n-hexane mixed solution to coagulate the resin. The coagulated resin was filtered, washed with a small amount of n-hexane, and dried under vacuum to obtain 20 g of a resin product.

The resin was confirmed to be a copolymer with a copolymerization molar ratio of the recurring unit (I-1), recurring unit (II), and recurring unit (V-1), shown in the following formula (19), of 30:20:50, and having Mw of 7,000. This resin is referred to as a "resin (A-4)".

[0165]

[Formula 47]



[0166]

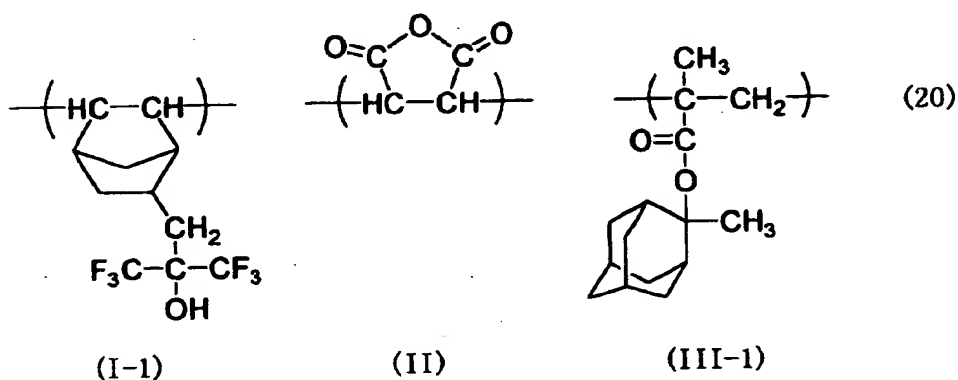
Synthesis Example 10

The same polymerization reaction as in the Synthesis Example 9 was carried out, except for using 12 g of 5-[2,2-bis(trifluoromethyl)-2-hydroxyethyl]bicyclo[2.2.1]-hept-2-ene, 4.3 g of maleic anhydride, and 8.7 g of 2-(2-methyl)adamantyl methacrylate as monomers, to obtain 19 g of a resin.

The resin was confirmed to be a copolymer with a copolymerization molar ratio of the recurring unit (I-1), recurring unit (II), and recurring unit (III-1), shown in the following formula (20), of 35:35:30, and having Mw of 6,800. This resin is referred to as a "resin (A-5)".

[0167]

[Formula 48]



[0168]

Synthesis Example 11

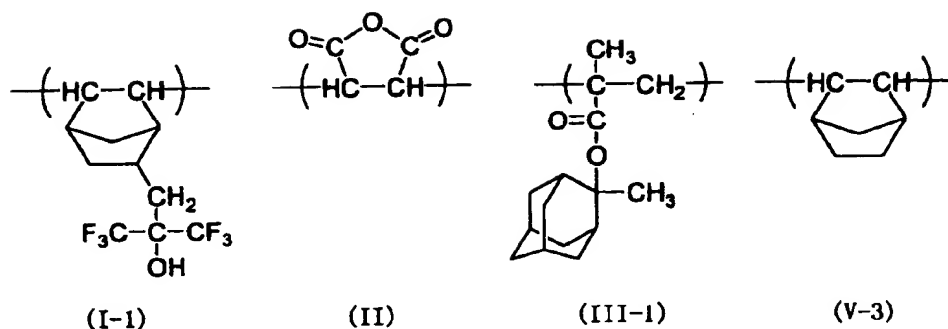
The same polymerization reaction as in the Synthesis Example 9 was carried out, except for using 11.5 g of 5-[2,2-bis(trifluoromethyl)-2-hydroxyethyl]bicyclo[2.2.1]hept-2-ene, 1.3 g of norbornene, 5.5 g of maleic anhydride, and 6.6 g of 2-(2-methyl)adamantyl methacrylate as monomers, to obtain 21 g of a resin.

The resin was confirmed to be a copolymer with a copolymerization molar ratio of the recurring unit (I-1), recurring unit (II), recurring unit (III-1), and recurring unit (V-3), shown in the following formula (21), of 30:10:40:20, and having Mw of 7,300. This resin is referred to as a "resin (A-6)".

[0169]

[Formula 49]

(21)



[0170]

Synthesis Example 12

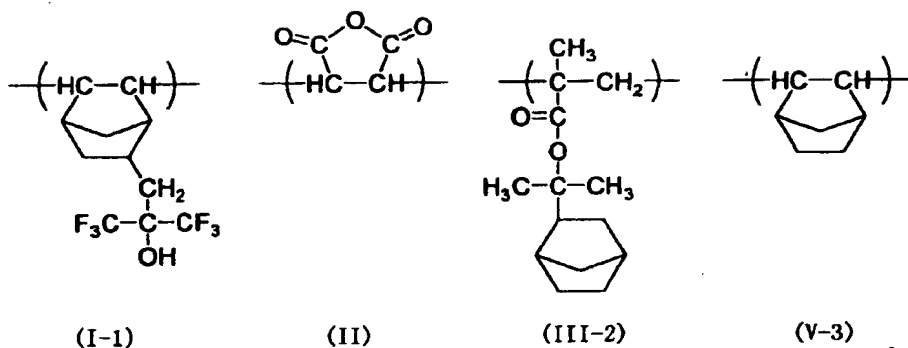
The same polymerization reaction as in the Synthesis Example 9 was carried out, except for using 11.8 g of 5-[2,2-bis(trifluoromethyl)-2-hydroxyethyl]bicyclo[2.2.1]-hept-2-ene, 1.4 g of norbornene, 5.6 g of maleic anhydride, and 6.4 g of 2-(2'-methacryloyloxy-2'-propyl)norbornene as monomers, to obtain 20 g of a resin.

The resin was confirmed to be a copolymer with a copolymerization molar ratio of the recurring unit (I-1), recurring unit (II), recurring unit (III-2), and recurring unit (V-3), shown in the following formula (22), of 30:10:40:20, and having Mw of 6,400. This resin is referred to as a "resin (A-7)".

[0171]

[Formula 50]

(22)



[0172]

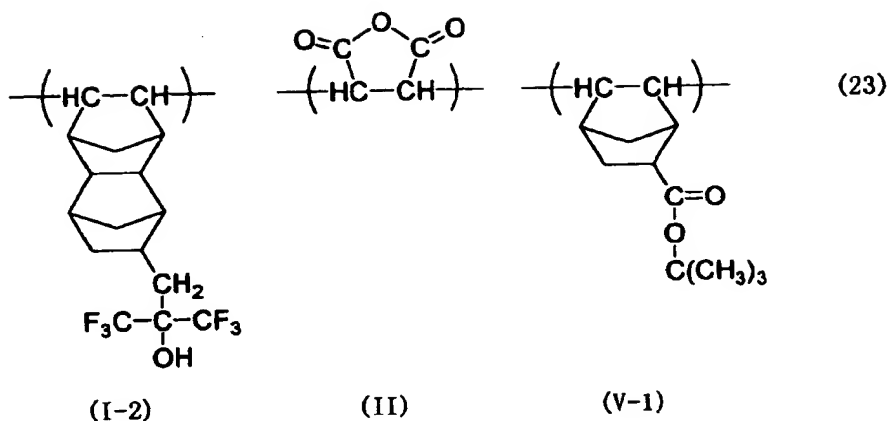
Synthesis Example 13

The same polymerization reaction as in the Synthesis Example 9 was carried out, except for using 9.7 g of 8-(2,2,2-trifluoro-1-trifluoromethyl-1-hydroxyethyl) tetracyclo[4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene, 8.3 g of 5-t-butoxycarbonylbicyclo[2.2.1]hept-2-ene, and 7 g of maleic anhydride as monomers, to obtain 21 g of a resin.

The resin was confirmed to be a copolymer with a copolymerization molar ratio of the recurring unit (I-2), recurring unit (II), and recurring unit (V-1), shown in the following formula (23), of 30:20:50, and having Mw of 7,100. This resin is referred to as a "resin (A-8)".

[0173]

[Formula 51]



[0174]

Synthesis Example 14

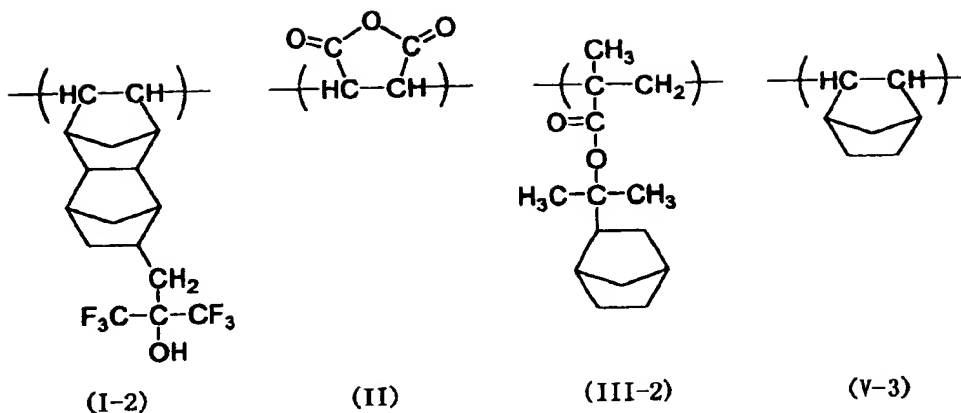
The same polymerization reaction as in the Synthesis Example 9 was carried out, except for using 12.3 g of 8-(2,2,2-trifluoro-1-trifluoromethyl-1-hydroxyethyl) tetracyclo[4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene, 0.6 g of norbornene, 4.2 g of maleic anhydride, and 8 g of 2-(2'-methacryloyloxy-2'-propyl)norbornene as monomers, to obtain 22 g of a resin.

The resin was confirmed to be a copolymer with a copolymerization molar ratio of the recurring unit (I-2), recurring unit (II), recurring unit (III-2), and recurring unit (V-3), shown in the following formula (24), of 30:10:40:20, and having Mw of 6,500. This resin is referred to as a "resin (A-9)".

[0175]

[Formula 52]

(24)



[0176]

Synthesis Example 15

(1) Polymerization

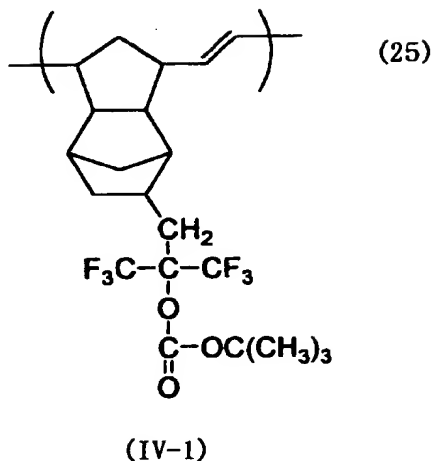
A separable flask equipped with a stirrer, a reflux condenser, and a three-way cock was charged with 100 parts by weight of 8-[2,2-bis(trifluoromethyl)-2-t-butoxycarbonyloxyethyl]tetracyclo[4.4.0.1^{2,5}.1^{7,10}]-dodec-3-ene, 33 parts by weight of 1-hexene (molecular weight modifier), and 200 parts by weight of toluene, and the mixture was heated to 80°C. Next, after the addition of 0.17 part by weight of a toluene solution of triethylaluminum (concentration: 1.5 mol/l) and 1.0 part by weight of a toluene solution of tungsten hexachloride (concentration: 0.05 mol/l) as a metathesis catalyst, the ring-opening polymerization reaction was carried out at 80°C for three hours while stirring to obtain a resin solution.

The resin was confirmed to be a polymer consisting of the recurring unit (IV-1) of the following formula (25) and

having Mw of 12,000 (yield 67 wt%). This resin is referred to as a "resin (A-10)".

[0177]

[Formula 53]



[0178]

(2) Hydrogenation

An autoclave was charged with 400 parts by weight of resin (A-10) and 0.075 part by weight of chlorohydrocarbonyltriphenylphosphine ruthenium as a hydrogenation catalyst. Hydrogenation reaction was carried out at 165°C under a hydrogen pressure of 100 kg/cm² · G for four hours.

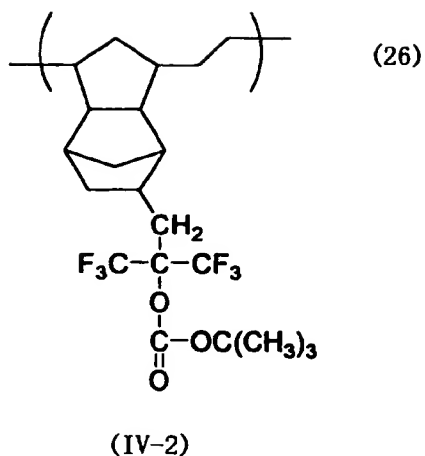
400 parts by weight of the resulting reaction solution and 100 parts by weight of toluene were charged to another reaction vessel. After the addition of 0.71 part by weight of lactic acid and 1.15 parts by weight of water, the mixture was stirred at 60°C for 30 minutes. Then, after the addition of 260 parts by weight of methanol, the mixture was further stirred

at 60°C for one hour. The reaction solution was cooled to room temperature and separated into a poor solvent layer (methanol layer) and a good solvent layer (resin solution layer). Only the poor solvent layer was removed. Methanol and toluene in the amount equivalent respectively to 4.5 wt% and 55 wt% of the removed methanol, were added to the reaction vessel, and the mixture was stirred at 60°C for one hour. Then, the reaction solution was again cooled to room temperature and separated into a poor solvent layer and a good solvent layer to remove only the poor solvent layer. This extraction procedure using methanol was repeated several times. The good solvent was removed from the finally obtained good solvent layer by evaporation, thereby collecting the resin. The resin was re-dissolved in tetrahydrofuran and a large amount of methanol was added to coagulate the resin. The coagulated resin was dried under reduced pressure to obtain a resin.

The degree of hydrogenation determined by the NMR spectrum was 100% and the resin was confirmed to be a polymer consisting of the recurring unit (IV-2) of the following formula (26). This resin is referred to as a "resin (A-11)".

[0179]

[Formula 54]



[0180]

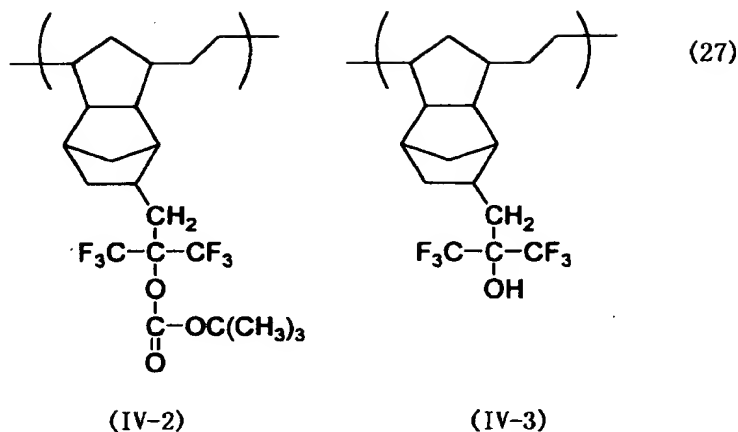
(3) Hydrolysis:

A flask was charged with 100 parts by weight of the resin (A-11), 200 parts by weight of propylene glycol monomethyl ether, 100 parts by weight of distilled water, and 1 part by weight of p-toluenesulfonic acid. Hydrolysis reaction was carried out for 8 hours while refluxing in a nitrogen atmosphere. The reaction solution was cooled to room temperature, neutralized by the addition of a large amount of water and triethylamine. The resin was extracted using ethyl acetate, and the extracted resin layer was washed with water until the water layer became neutral. The solvent was evaporated to obtain a resin.

The degree of hydrolysis determined by IR spectrum was 60%, and the resin was confirmed to be a copolymer with a copolymerization molar ratio of the recurring unit (IV-2) and recurring unit (IV-3), shown in the following formula (27), of 40:60. This resin is referred to as a "resin (A-12)".

[0181]

[Formula 55]



[0182]

Synthesis Example 16

(1) Polymerization

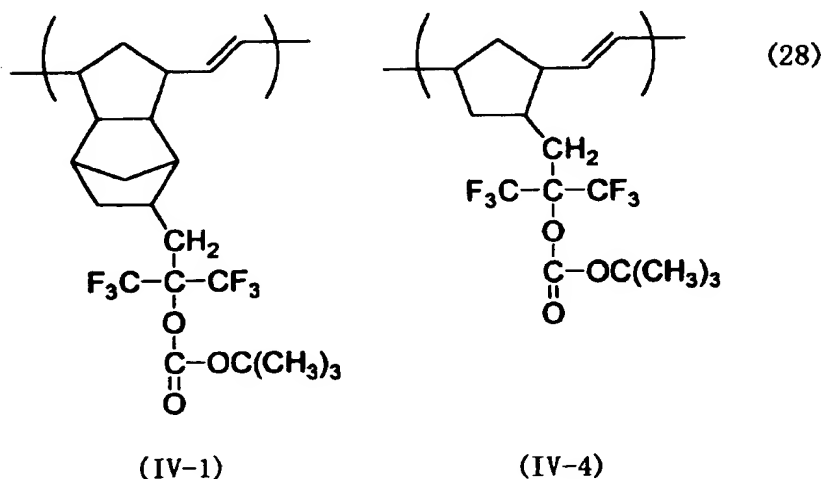
A separable flask equipped with a stirrer, a reflux condenser, and a three-way cock was charged with 60 parts by weight of 8-[2,2-bis(trifluoromethyl)-2-t-butoxycarbonyloxyethyl]tetracyclo[4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene, 40 parts by weight of 5-[2,2-bis(trifluoromethyl)-2-t-butoxycarbonyloxyethyl]bicyclo[2.2.1]hept-2-ene, 25 parts by weight of 1-hexene (molecular weight modifier), 400 parts by weight of 1,2-dichloroethane, and 0.6 part by weight of a chlorobenzene solution of triethylaluminum (concentration: 1.5 mol/l) and 4 parts by weight of a chlorobenzene solution of tungsten hexachloride (concentration: 10.025 mol/l) as a metathesis catalyst. The ring-opening polymerization reaction was carried out at 80°C for three hours. After the polymerization reaction, a large amount of methanol was added to the reaction solution to cause the resin to coagulate. The coagulated resin

was filtered and dried under vacuum to obtain a resin (yield: 92 wt%).

The resin was confirmed to be a copolymer with a copolymerization molar ratio of the recurring unit (IV-1) and recurring unit (IV-4), shown in the following formula (28), of 50:50, and having Mw of 13,000. This resin is referred to as a "resin (A-13)".

[0183]

[Formula 56]



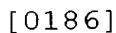
[0184]

(2) Hydrogenation

A hydrogenation reaction was carried out in the same manner as in Synthesis Example 15 using the resin (A-13).

The degree of hydrogenation determined by the IR spectrum and NMR spectrum was 100% and the resin was confirmed to be a copolymer consisting of the recurring unit (IV-2) recurring unit (IV-5) of the following formula (29). This resin is referred to as a "resin (A-14)".

[Formula 57]

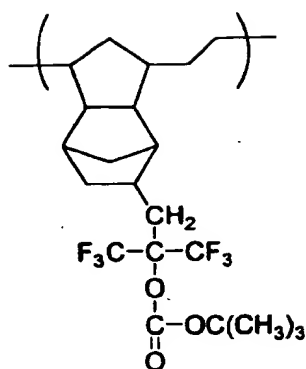


A hydrolysis reaction was carried out in the same manner as in Synthesis Example 15 using the resin (A-14).

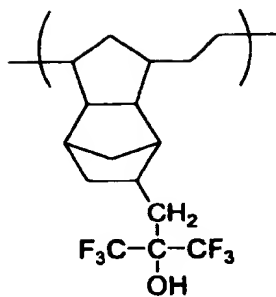
[0187]

[Formula 58]

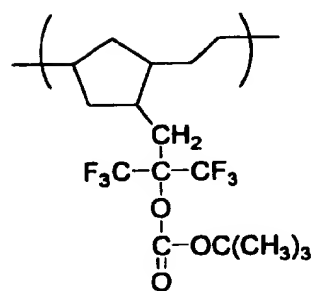
(30)



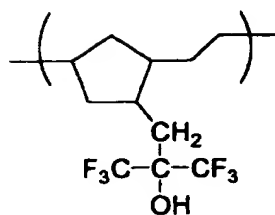
(IV-2)



(IV-3)



(IV-5)



(IV-6)

[0188]

Synthesis Example 17

(1) Polymerization

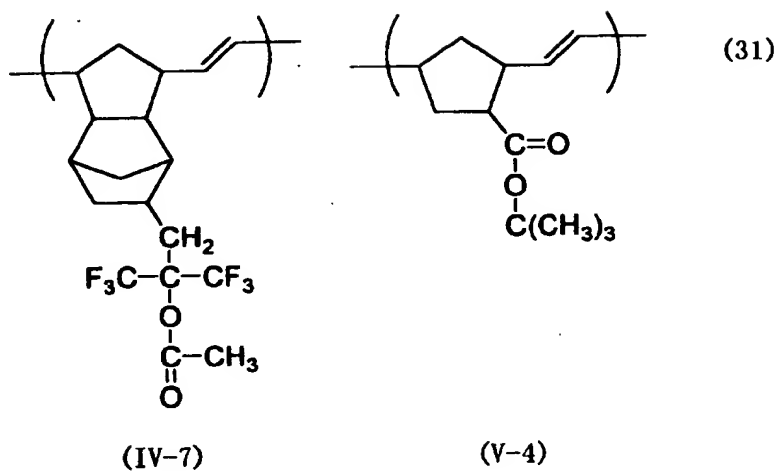
The same ring-opening polymerization reaction as in the Synthesis Example 16 was carried out, except for using 50 parts by weight of 8-[2,2-bis(trifluoromethyl)-2-methylcarbonyloxyethyl]tetracyclo[4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene and 50 parts by weight of 5-t-butoxycarbonylbicyclo[2.2.1]hept-2-ene.

The resulting resin was confirmed to be a copolymer with a copolymerization molar ratio of the recurring unit (IV-7) and recurring unit (V-4), shown in the following formula (31), of

40:60, and having Mw of 13,000. This resin is referred to as a "resin (A-16)".

[0189]

[Formula 59]



[0190]

(2) Hydrogenation

A hydrogenation reaction was carried out in the same manner as in Synthesis Example 15 using the resin (A-16).

The degree of hydrogenation determined by the IR spectrum and NMR spectrum was 100% and the resin was confirmed to be a copolymer consisting of the recurring unit (IV-8) recurring unit (V-5) of the following formula (32). This resin is referred to as a "resin (A-17)".

[0191]

[Formula 60]



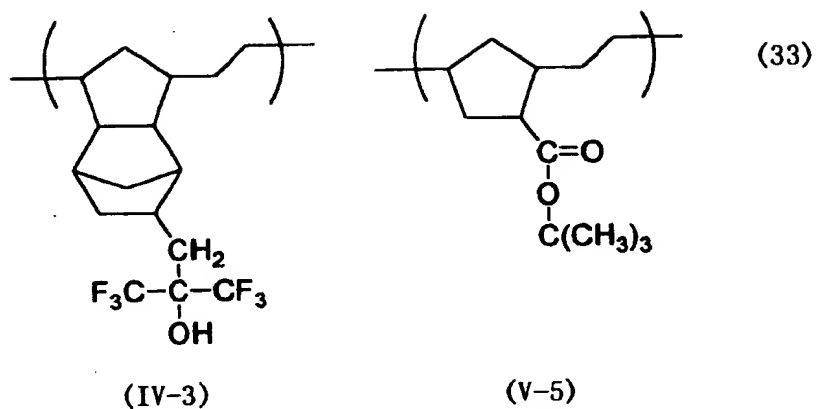
(3) Hydrolysis:

The degree of hydrolysis of methylcarbonyloxy groups determined by the IR spectrum was 100% and the resin was confirmed to be a polymer consisting of the recurring unit (IV-3) recurring unit (V-5) of the following formula (33). This

resin is referred to as a "resin (A-18)".

[0193]

[Formula 61]



[0194]

[Examples]

Examples 1-12 and Comparative Example 1

Each composition solution having components shown in Table 1 was evaluated. The evaluation results are shown in Table 3.

Components other than the resins (A-1) to (A-9), (A-12), (A-15), and (A-18) shown in Table 1 are as follows.

Other resins

a-1: t-Butyl methacrylate/methyl methacrylate/methacrylic acid copolymer (copolymerization molar ratio = 40/40/20, Mw = 20,000)

Acid generator (B)

B-1: Triphenylsulfonium nonafluoro-n-butanesulfonate

B-2: Bis(4-t-butylphenyl)iodonium nonafluoro-n-

butanesulfonate

B-3: 1-(3,5-dimethyl-4-hydroxyphenyl)tetrahydro-
thiopheniumnonafluoro-n-butanesulfonate

B-4: Bis(4-t-butylphenyl)iodonium perfluoro-n-
octanesulfonate

B-5: Nonafluoro-n-butanesulfonylbicyclo[2.2.1]hept-5-
ene-2,3-dicarbodiimide

Acid diffusion control agent

C-1: Tri-n-octylamine

C-2: 3-Pyperidino-1,2-propanediol

C-3: N-t-butoxycarbonyldicyclohexylamine

C-4: N-t-butoxycarbonyl-2-phenylbenzimidazole

Other additives

D-1: t-Butyl deoxycholate

D-2: Di-t-butyl 1,3-adamantanedicarboxylate

D-3: t-Butoxycarbonylmethyl deoxycholate

Solvent

E-1: 2-Heptanone

E-2: Cyclohexanone

[0195]

[Table1]

Unit in parentheses (part by weight)

| | Resin | Photoacid generator (B) | Acid diffusion controller | Other additives | Solvents |
|-----------------------|-----------|-------------------------|---------------------------|-----------------|------------------------|
| Example 1 | A-1 (90) | B-1 (2.0) | C-2 (0.05) | D-1 (10) | E-1 (430) E-2 (100) |
| Example 2 | A-2 (90) | B-2 (2.0) | C-3 (0.10) | D-2 (10) | E-1 (430) E-2 (100) |
| Example 3 | A-3 (90) | B-4 (3.0) | C-4 (0.10) | D-2 (10) | E-1 (430) E-2 (100) |
| Example 4 | A-4 (90) | B-3 (3.5) | C-4 (0.10) | D-3 (10) | E-1 (430) E-2 (100) |
| Example 5 | A-5 (90) | B-2 (3.0) | C-2 (0.05) | D-3 (10) | E-1 (430) E-2 (100) |
| Example 6 | A-6 (90) | B-4 (3.0) | C-3 (0.10) | D-2 (10) | E-1 (430) E-2 (100) |
| Example 7 | A-7 (90) | B-4 (3.0) B-5 (2.0) | C-3 (0.10) | D-3 (10) | E-1 (430) E-2 (100) |
| Example 8 | A-8 (90) | B-2 (3.0) B-5 (2.0) | C-4 (0.10) | D-3 (10) | E-1 (430) E-2 (100) |
| Example 9 | A-9 (90) | B-1 (2.0) | C-2 (0.05) | D-2 (10) | E-1 (430) E-2 (100) |
| Example 10 | A-12 (90) | B-2 (3.0) | C-4 (0.10) | D-1 (10) | E-1 (430) E-2 (100) |
| Example 11 | A-15 (90) | B-4 (3.0) B-5 (2.0) | C-4 (0.10) | D-3 (10) | E-1 (430) E-2 (100) |
| Example 12 | A-18 (90) | B-4 (3.0) | C-3 (0.05) C-4 (0.05) | D-2 (10) | E-1 (430) E-2 (100) |
| Comparative Example 1 | a-1 (90) | B-1 (2.0) | C-1 (0.05) | D-1 (10) | E-1 (530) |

[0196]

[Table 2]

| | Thickness of resist (μm) | Substrate | PB | | PEB | |
|-----------------------|---------------------------------------|-----------|------------------------------|------------|------------------------------|------------|
| | | | Temp. ($^{\circ}\text{C}$) | Time (sec) | Temp. ($^{\circ}\text{C}$) | Time (sec) |
| Example 1 | 0.4 | ARC | 130 | 90 | 140 | 90 |
| Example 2 | 0.4 | ARC | 130 | 90 | 140 | 90 |
| Example 3 | 0.4 | ARC | 130 | 90 | 140 | 90 |
| Example 4 | 0.4 | ARC | 130 | 90 | 140 | 90 |
| Example 5 | 0.4 | ARC | 130 | 90 | 140 | 90 |
| Example 6 | 0.4 | ARC | 130 | 90 | 140 | 90 |
| Example 7 | 0.4 | ARC | 130 | 90 | 140 | 90 |
| Example 8 | 0.4 | ARC | 130 | 90 | 140 | 90 |
| Example 9 | 0.4 | ARC | 130 | 90 | 140 | 90 |
| Example 10 | 0.4 | ARC | 130 | 90 | 140 | 90 |
| Example 11 | 0.4 | ARC | 130 | 90 | 140 | 90 |
| Example 12 | 0.4 | ARC | 130 | 90 | 140 | 90 |
| Comparative Example 1 | 0.4 | ARC | 130 | 90 | 140 | 90 |

[0197]

[Table 3]

| | Transmittance (193 nm, %) | Sensitivity (J/m ²) | Resolution (μ m) | Developing Defects | Pattern Configuration |
|--------------------------|------------------------------|------------------------------------|--------------------------|-----------------------|--------------------------|
| Example 1 | 75 | 73 | 0.15 | 0 | Good |
| Example 2 | 72 | 74 | 0.15 | 0 | Good |
| Example 3 | 69 | 69 | 0.15 | 0 | Good |
| Example 4 | 71 | 70 | 0.15 | 0 | Good |
| Example 5 | 68 | 74 | 0.15 | 0 | Good |
| Example 6 | 73 | 72 | 0.15 | 0 | Good |
| Example 7 | 70 | 68 | 0.15 | 0 | Good |
| Example 8 | 75 | 77 | 0.15 | 0 | Good |
| Example 9 | 70 | 69 | 0.15 | 0 | Good |
| Example 10 | 68 | 71 | 0.15 | 0 | Good |
| Example 11 | 70 | 74 | 0.15 | 0 | Good |
| Example 12 | 71 | 71 | 0.15 | 0 | Good |
| Comparative Example 1 | 62 | 150 | 0.18 | 45 | Good |

[0198]

[Effect of the Invention]

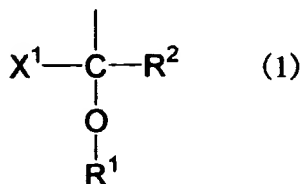
The radiation-sensitive resin composition of the present invention has high transmittance of radiation, exhibits superior basic properties as a chemically amplified resist such as high sensitivity, resolution, and pattern shape, and is capable of producing semiconductors at a high yield without producing developing defects during microfabrication. The resin composition is expected to be an ideal material in the semiconductor device field in which microfabrication technology will further advance in the future.

[Document Name] Abstract

[Abstract]

[Subject] To provide a resin composition that exhibits high transmittance of radiation, high sensitivity, resolution, and pattern shape, and is useful as a chemically amplified resist in producing semiconductor devices at a high yield.

[Means for the Solution] A radiation-sensitive resin composition comprising (A) an acid-dissociating group-containing resin having a structure of the following formula (1) and (B) a photoacid generator



wherein R¹ represents a hydrogen atom, a monovalent acid-dissociating group, an alkyl group which does not have an acid-dissociating group, or an alkylcarbonyl group which does not have an acid-dissociating group, X¹ represents a linear or branched fluorinated alkyl group having 1-4 carbon atoms, and R² represents a hydrogen atom, a linear or branched alkyl group, or a linear or branched fluorinated alkyl group.

[Selected Drawings] None

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HISTORICAL INFORMATION ON APPLICANT

- Identification No. [000004178]

1. Date of Alteration December 10, 1997

- [Reason for Alteration] Alteration of Name

Address: 2-11-24, Tsukiji, Chuo-ku, Tokyo

Name: JSR Corporation

Certificate No. 2001-3053110

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ASSIGNMENT

April 4, 2001

Address Armonk, New York 10504, United States of America
Assignee INTERNATIONAL BUSINESS MACHINES CORPORATION
(Jeffrey L. Forman, Representative)

Address 2-11-24, Tsukiji,
Chuo-ku, Tokyo
Assignor JSR Corporation
Eiichi MATSUMOTO,
Representative

The Assignor hereby confirms that partial right to obtain a Patent for the below identified invention has been assigned to the above-identified Assignee.

Patent Application No. 182297/2000
Title of Invention RADIATION-SENSITIVE RESIN COMPOSITION

Certificate No. 2001-3053110